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THE VALUATION OF SACCHARIN.

BY E. EMMET REID.

About two years ago, at the suggestion of Prof. Remsen, I took up the study of the hydrolysis of acid amides.[1] This was suggested by the work of Remsen and Burton[2] on saccharin, in which it appeared that benzoic sulphinide, when boiled with dilute acids, passes through *o*-sulphaminebenzoic acid into the acid ammonium salt of *o*-sulphobenzoic acid, while *p*-sulphaminebenzoic acid is not affected. In my work it has been customary to estimate the amount of amide decomposed by the amount of ammonia it would yield. From this it was natural to attempt the estimation of benzoic sulphinide in the same way. A number of analyses were made of a specimen of commercial saccharin. In these, 0.750 gram saccharin was boiled with dilute hydrochloric acid and the ammonia determined by distilling with alkali. At first the results were not quite satisfactory. As Hefelmann's[3] work had been brought to my notice it seemed worth while to try 71 per cent sulphuric acid as recommended by him for the hydrolysis.

After making a few analyses with sulphuric acid, I was fortunate in securing the cooperation of Mr. L. B. Mat-

[1] This JOURNAL, **19**, 319. [2] *Ibid.*, **11**, 403.
[3] Ph. C., **85**, 107; and Ph. C., 1895, No. 16.

tern of this laboratory, an experienced and careful analyst who, for some time past, had been engaged under Professor Remsen's direction, on a comparison of the methods of Remsen and Burton and of Hefelmann. In all of the analyses with sulphuric acid, Mr. Mattern had charge of all except the distillation and titration.

As 1 cc. of the standard acid in hand was equivalent to 26 mg. sulphinide, 26 × 25 or 650 mg. saccharin was taken for each analysis. Then it was only necessary to multiply by 4 the number of cubic centimeters of acid neutralized by the ammonia, in order to obtain the percentage of sulphinide in the sample.

Method of Analysis with Sulphuric Acid.

To 0.650 gram saccharin weighed into a test-tube about 18×160 mm., was added 10 cc. of 71 per cent sulphuric acid, made by diluting 132 grams pure concentrated acid with 37 cc. of water. The test-tube was loosely closed by a cork through which passed a small glass rod, bent into a loop at the bottom. By means of this the mixture was repeatedly stirred during the three hours' heating. Eight to sixteen of these tubes were suspended in a bath of vigorously boiling water, for three hours. After cooling, the contents of the tube were diluted with water, washed into the distilling flask, 15 grams caustic soda added, and the ammonia distilled off into standard acid.

Results Stated in Percentages of Benzoic Sulphinide.

Sample A—Commercial Saccharin.

1	54.5	9	55.1	16	55.3	23	55.3
2	54.9	10	55.5	17	55.7	24	55.4
3	54.5	11	55.1	18	55.1	25	55.4
4	55.1	12	55.6	19	55.4	26	55.7
5	55.8	13	55.6	20	55.1	27	54.8
6	55.3	14	55.6	21	55.2	28	55.3
7	55.6	15	55.2	22	55.1	29	55.2
8	55.7						

Nos. 1–4 were experimental. Nos. 20–29 were made entirely by Mr. Mattern with independent standard solutions.

He had previously found 55.2 and 54.7 per cent by Hefelmann's method.

Sample B—Another Lot of Commercial Saccharin.

1	94.0	5	94.5	9	95.1
2	94.3	6	94.3	10	95.1
3	94.1	7	95.3	11	95.0
4	94.4	8	94.5	12	94.9

Sample C—4.600 Grams Pure Sulphinide, Crystallized from Acetone, Mixed with 0.0700 Gram Pure Parasulphaminebenzoic Acid.

Calculated, 86.8 per cent.

	Found.		Found.
1	88.0	4	88.0
2	86.7	5	86.7
3	87.4	6	87.5

Sample D—4.000 Grams Pure Sulphinide Mixed with 1.500 Grams Pure Parasulphaminebenzoic Acid.

Calculated 72.7 per cent.

	Found.		Found.
1	72.5	5	72.9
2	73.6	6	73.3
3	73.3	7	73.6
4	73.5	8	73.1

Sample E—A Beautiful Specimen of Commercial Saccharin.

	Found.		Found.
1	98.7	5	98.9
2	99.1	6	99.3
3	98.5	7	98.9
4	98.8	Av.	98.9

Sample F—Another Specimen of Commercial Saccharin.

	Found.		Found.
1	89.0	4	89.2
2	89.4	5	88.6
3	89.6		

Sample G—Pure Benzoic Sulphinide from Acetone.

	Found.		Found.
1	99.1	4	99.7
2	99.7	5	98.8
3	98.9	Av.	99.2

The following mixtures were made up from pure sulphinide and pure parasulphaminebenzoic acid:

No.	Sulphinide. Gram.	Para Acid. Gram.	Per cent calc.	Per cent found.
1	0.5291	0.1209	81.4	82.2
2	0.5328	0.1172	82.0	82.0
3	0.4971	0.1529	76.5	79.1
4	0.5197	0.1303	79.9	80.9
5	0.5026	0.1474	77.3	78.9
6	0.5036	0.1464	77.5	78.1
7	0.5316	0.1184	81.8	81.7
8	0.3381	0.3119	52.0	53.5
9	0.3431	0.3069	52.8	53.5
10	0.3518	0.2982	54.1	55.2
11	0.4194	0.2306	64.5	62.4
12	0.4168	0.2332	64.1	64.6
13	0.5208	0.1292	80.2	79.6

Experiments with Pure Parasulphaminebenzoic Acid.

The acid used in these, as in other analyses in this work, was kindly furnished me by Mr. J. S. Chamberlain, of this laboratory, who has for some time past been investigating that substance. The sample was considered by him to be absolutely pure.

0.300 gram pure parasulphaminebenzoic acid was weighed into each of eight test-tubes, heated in the usual manner with 71 per cent sulphuric acid, and distilled with caustic soda. The results are given in cubic centimeters of $\frac{1}{7}$ N acid.

1	0.27
2	0.19
3	0.27
4	0.27
5	0.29
6	0.29
7	0.27
8	0.27
Blank	0.05

Average minus blank, 0.21 cc. equivalent to 0.51 mg. ammonia, or 5.9 mg. parasulphamine acid.

These results seem to show that parasulphaminebenzoic acid is slightly hydrolyzed by 71 per cent sulphuric acid at 100° C. This is supported by the generally high results of the test mixtures above.

Several other samples of pure parasulphaminebenzoic acid with 71 per cent sulphuric acid were overheated by the water-

bath accidentally going dry. In one of these, 86 per cent of the acid was found to be hydrolyzed. These results led me to return to hydrochloric acid and to devise the method described below.

Method of Analysis.

0.650 gram saccharin is weighed into a 100 cc. Florence flask and 50 cc. dilute hydrochloric acid added. This acid is prepared by diluting 120 cc. pure concentrated hydrochloric acid to 1 liter. The flask is fitted with a cork through which passes a glass tube 8 mm. wide and 45 cm. long. The flask is placed on a sand-bath and allowed to boil gently for two hours. Eight of these flasks can be heated conveniently on one sand-bath and require only occasional attention. The stopper is removed and the solution allowed to evaporate down to about 10 cc. After diluting, the contents of the flask are washed into the usual distilling flask and 20 cc. added of a solution containing 0.5 gram caustic soda in 1 cc. (or 10 grams of caustic soda). The ammonia is distilled off into standard acid and the excess titrated back with aqueous caustic potash, cochineal being used as indicator. After neutralizing, 0.20 or 0.30 cc. standard acid is added and the neutral point again determined, the two results being averaged. For a distilling flask, a 500 cc. pear-shaped digesting flask serves best. Steam is passed in from a large flask containing water with a little potassium bichromate and sulphuric acid. The steam is a great advantage, as it causes even very concentrated solutions of caustic soda loaded with salts to boil nicely. In nearly a thousand analyses carried on with these flasks with steam only two have broken.

Standard acid about $\frac{1}{4}$ N is the most convenient. 25 cc. of this is put into the receiver each time. If the saccharin is known to be of low grade less may be used.

The following analyses were made by this method :

Sample H—Pure Benzoic Sulphinide.

Prepared in exactly the same way as Sample G. Both prepared by Mr. Mattern.

1	100.8	5	99.3
2	100.4	6	99.4
3	100.6	7	100.2
4	100.5	Av.	100.2

No. 5 went to dryness with the hydrochloric acid.

The excess over 100 per cent is due to ammonia in the reagents and to errors of burettes, etc. When calculated for nitrogen, No. 1 appears thus:

	Calculated.	Found.
N	7.65	7.71

It is important to notice that the average is just 1 per cent higher than was found for Sample G with sulphuric acid.

The same burettes, standard solutions, etc., were used in both cases. It seems fair to conclude that by the above treatment with hydrochloric acid benzoic sulphinide is more completely hydrolyzed, and yields more ammonia than when heated with 71 per cent sulphuric acid at 100° C. for three hours.

The following test mixtures were made up and analyzed. Into each was weighed 500 mg. sulphinide and 150 mg. para acid:

Calculated, 76.9.

	Found.		Found.
1	77.6	5	76.4
2	77.4	6	77.6
3	77.5	7	77.4
4	77.2		

Into each was weighed 450 mg. sulphinide and 200 mg. para acid.

Calculated, 69.2.

	Found.		Found.
1	69.2	5	68.8
2	69.3	6	68.4
3	69.0	7	69.1
4	69.3	8	69.1

Sample A—Commercial Saccharin.

	Found.		Found.
1	54.6	6	54.1
2	54.2	7	54.0
3	54.1	8	54.4
4	55.0	9	54.2
5	54.2	Av.	54.3

These results are on the average 1 per cent lower than those obtained with sulphuric acid, which must have converted a little of the large amount of para acid present.

Sample I—Commercial Saccharin from the Same Can as B, but from Another Part of the Can.

1	76.7	5	76.2
2	77.2	6	74.9
3	77.3	7	76.2
4	76.9	8	76.4

Sample J—Commercial Saccharin.

1	99.0	4	99.2
2	98.6	5	99.7
3	98.8	6	99.0

Sample K—Commercial Saccharin.

(Only 1.23 gram in hand.)

1	96.9	2	96.7

Sample E—Commercial Saccharin.

1	99.7	5	99.9
2	99.7	6	99.7
3	99.8	7	99.2
4	99.8	Av.	99.7

Here the average is 0.8 per cent higher than average of analyses of same sample with sulphuric acid. Compare analyses of pure saccharin.

Experiments with Pure Parasulphaminebenzoic Acid.

0.300 gram of the pure acid weighed into each of six flasks, heated in the usual manner with hydrochloric acid and distilled with 10 grams caustic soda. The results are given in cubic centimeters of $\frac{1}{7}$ N acid neutralized.

1	0.02	5	0.04
2	0.02	6	0.05
3	0.02	7	0.04
4	0.02	8	0.05

Average 0.03 cc. Blank with reagents 0.03 cc. Parasulphaminebenzoic acid is not acted upon by hydrochloric acid under these conditions.

Experiments were next undertaken to determine the approximate rate of hydrolysis and to test the completeness of the reaction when carried on according to Remsen and Burton. 0.650 gram of a sample of commercial saccharin was weighed into each of eight flasks, with 50 cc. of dilute acid (1 part of pure concentrated hydrochloric acid to 8 parts water). The six flasks were placed on a sand-bath and began to boil at nearly the same time:

No. 1	boiled about thirty-three minutes,	found	69.3
" 2	" " forty-five "	"	81.6
" 3	" " sixty "	"	84.5
" 4	" " " "	"	87.0
" 5	boiled about 60 minutes and evapora-		93.6
" 6	ted down to 10 cc.		93.5

Analyses of the same specimen by the usual method gave about 94 per cent. The hydrolysis was complete in 5 and 6. Remsen and Burton boiled 2 grams saccharin with 200 cc. of this strength hydrochloric acid and evaporated down to 15 cc., which was more thorough treatment than Nos. 5 and 6 received. From these experiments I am unable to account for the fact that Hefelmann found only about 93 per cent, as much ammonia by the method of Remsen and Burton as by his own.

Action of Caustic Soda on Saccharin.

Boiling caustic soda solution quite readily converts benzoic sulphinide into the sodium salt of *o*-sulphaminebenzoic acid but does not break this acid down. In twelve experiments boiling 650 mg. of Sample A, a very low grade specimen, with 10 grams caustic soda in from 75 to 150 cc. of water, for one and a half to two hours, only a few tenths of a milligram of ammonia was found in each case. This was probably not due to the benzoic sulphinide present. This was shown by boiling 650 mg. of Sample E in the same way by which only 0.05 mg. ammonia was found. This is about the amount found in a blank. To the residue in the distilling flask an excess of hydrochloric acid was added and the whole boiled for several hours and evaporated down. As the solution contained much sodium chloride there was a little spattering, but on adding an excess of caustic soda and

distilling, an amount of ammonia corresponding to 98.5 per cent sulphinide was found. Previous analysis in the usual way gave 99.7 per cent. This is of importance, as it suggests that the sulphinide may be estimated, with fair accuracy, in the presence of salts of ammonia or of other volatile bases or of benzamide, and many of its substitution-products, of amides of fatty acids, or of anything else which is readily broken down by boiling with 10 or 15 per cent caustic soda.

To test this the following experiment was made. Unfortunately, it was not very successful and would have been repeated but for lack of time. The following mixture was made up: 0.1478 gram pure ammonium chloride, 0.5000 gram pure *p*-nitrobenzamide, 0.6500 gram pure benzoic sulphinide, 0.3750 gram pure *p*-sulphaminebenzoic acid, 4 grams magnesium chloride, and 0.5 gram caustic soda were added and the whole distilled.

	Calculated. mg.	Found.
NH_3	47.1	47.9

5 grams caustic soda added and distilled again. Found 51.1 mg. NH_3, corresponding to 499 mg. out of 500 mg. *p*-nitrobenzamide. The contents of the flask were neutralized with hydrochloric acid and about 8 cc. of concentrated hydrochloric acid added. The solution was boiled for several hours and allowed to evaporate down. An excess of caustic soda was added and the ammonia distilled off. This was found to correspond to 99.1 per cent of the saccharin put in. The flask was removed, an excess of pure sulphuric acid added and heated. Unfortunately, it was heated too high, so that slight charring took place, and not only the parasulphaminebenzoic acid was broken down but some little of the *p*-nitrobenzoic acid was also acted upon. On adding excess of caustic soda and distilling, 36.2 mg. ammonia was obtained instead of 33.7 mg. ammonia, representing the para acid. Had this not been overheated it would have been possible to have estimated the nitrogen in the nitro-group by the Kjeldahl process. Hence there are, at least, five classes of nitrogen compounds, of which the above are representatives, the nitrogen of which can be successively and independently estimated in the same solution. This suggests the inorganic groups.

Analysis of Pure Parasulphaminebenzoic Acid.

To hydrolyze this acid completely it is unnecessary to use any of the modifications of the Kjeldahl process. Heating with pure concentrated sulphuric acid alone is sufficient.

0.3000 gram of the pure parasulphaminebenzoic acid was weighed into each of the two test-tubes. To each was added 5 cc. pure concentrated sulphuric acid. The two tubes were placed in a beaker containing sulphuric acid and heated several hours at from 230°–260° C. The contents of the tubes were distilled with caustic soda in the usual way and gave (1) 25.73 mg. ammonia and (2) 25.57 mg. ammonia. Subtracting 0.12 mg., the amount of ammonia found with nearly the same amount of reagents, these figures give:

1. 8.54 per cent NH_3.
2. 8.49 per cent NH_3.

Calc. 8.46 per cent NH_3.

It seems likely that the hydrolysis might be complete at a much lower temperature. By heating with concentrated sulphuric acid alone and only to such temperature as might be found sufficient, parasulphaminebenzoic acid might be estimated in the presence of many nitrogenous bodies.

General Remarks.

One advantage in the use of hydrochloric acid is that, from first to last, during the heating the whole sample of saccharin is completely in solution, and much more uniform and certain action may be expected. While the use of hydrochloric acid is preferred yet the 71 per cent sulphuric acid, when used as above directed, gives very nearly the same results.

The estimation of sulphinide according to this method is much simpler and quicker than the ordinary Kjeldahl analysis for nitrogen and seems capable of the same proportionate accuracy.

As the percentage of nitrogen is multiplied by 13 to obtain the percentage of sulphinide, the absolute error is multiplied by the same factor. As a variation of 0.2 per cent on 100 per cent, or 1 part in 500 is allowable, it is useless to weigh the sample of saccharin with great accuracy. 0.2 or 0.3 of a

milligram either way makes little difference. I have weighed 8 samples of 0.650 gram ±0.0003 gram in sixteen minutes. To hydrolyze 10 grams saccharin according to Hefelmann, filter, wash, dilute to 500 cc., and measure out portions for the estimation of ammonia, is certainly more troublesome. The weight of sample taken, strength of solutions, etc., are not essential to the method but are capable of wide variation. It is hoped that what has been done may lead to the more general and accurate valuation of commercial saccharin as well as to the detection and estimation of saccharin in many substances, both liquid and solid, in which this substance might be used. The method in one form or another seems capable of wide application, but the limits and conditions of its use must yet be determined.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
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Contributions from the Chemical Laboratory of the University of Minnesota.

SOME DERIVATIVES OF CAMPHOROXIME.

BY G. B. FRANKFORTER AND A. D. MAYO.

As stated by Naegli,[1] camphoroxime forms derivatives characteristic of the common acetoximes, differing, however, by their unusual stability and by their tendency to crystallize. Of the derivatives, the hydrochloride, $C_{10}H_{18}NOH.HCl$, the sodium salt, $C_{10}H_{18}NONa$, and the ethyl ester, $C_{10}H_{18}NOC_2H_5$, were prepared. No derivatives, however, were made from the acids, the oxime remaining unchanged even with the strong mineral acids. With the organic acid chlorides, a peculiar reaction was observed, the result of which was the formation of hydrochloric acid, acetic acid, and camphornitril or so-called anhydride, according to the following equation:

$$C_{10}H_{18}NOH + CH_3COCl = C_{10}H_{18}N + CH_3COOH + HCl.$$

This so-called anhydride is a liquid at the ordinary temperature, with an agreeable odor and a boiling-point of 216° to 218° C. It changes to campholenic acid according to the common nitril reaction.

With acid anhydrides, the same tendency to break off a

[1] Bei. d. chem. Ges., 16, 2981.

molecule of water, was observed by the characteristic odor of the nitril. However, if conditions are favorable, they form esters, all of which show a greater or less tendency to break down into the nitril.

Acetylcamphoroxime, $C_{10}H_{14}NO(CH_3CO)$.[1]—Acetic anhydride reacts upon camphoroxime readily. If heated with excess, it forms the nitril as indicated by the odor and by the boiling-point:

$$C_{10}H_{14}NOH + (CH_3CO)_2O = C_{10}H_{15}N + 2CH_3COOH.$$

If, however, the oxime is treated with the anhydride and allowed to stand for some time in a desiccator, the almost pure ether is formed:

$$C_{10}H_{14}NOH + (CH_3CO)_2O = C_{10}H_{14}NO(CH_3CO) + CH_3COOH.$$

The purified substance has an aromatic odor and the boiling-point, 170° C, decomposing and turning black at that temperature. The oil is insoluble in water, but slowly decomposes, forming acetic acid and the oxime. With sodium hydroxide the substance readily saponifies, forming sodium acetate and the sodium salt of the oxime:[2]

$$C_{10}H_{14}NO(CH_3CO) + 2NaOH = C_{10}H_{14}NONa + CH_3COONa + H_2O.$$

By carefully neutralizing the sodium salt with hydrochloric acid camphoroxime is liberated. Analysis of the purified substance gave the following results:

I. 0.1866 gram of the substance gave 0.4688 gram CO_2, and 0.1554 gram H_2O.

II. 0.2338 gram of the substance gave 0.5862 gram CO_2, and 0.2156 gram H_2O.

	Calculated for $C_{10}H_{14}NO(CH_3CO)$.	Found. I.	Found. II.
C	68.89	68.52	68.39
H	9.09	9.25	10.24

Chloralcamphoroxime, $(C_{10}H_{14}NO)_2CHCCl + 2H_2O$.—Camphoroxime treated with chloral alone evidently forms several different substances. If, however, the chloral be added to an ether solution of the oxime and allowed to stand until the

[1] Proc. Chem. Soc., 1897, 135.

[2] Part of Thesis presented by A. D. Mayo for M. S. degree, 1896.

ether has evaporated, a waxy substance remains, which, when stirred with an excess of water, readily becomes a solid, crystalline mass. Purified from alcohol, the substance formed a fine, white, crystalline powder, melting at 82°. It decomposes at the same temperature, and is likewise readily broken up by alkalies. It contains water of crystallization, all of which cannot be removed without decomposition. It decomposes slowly on standing over sulphuric acid. It is inodorous but has the taste of camphor. It is soluble in ether and alcohol, but insoluble in water. An analysis gave the following :

0.2427 gram of the substance gave 0.4748 gram CO_2, and 0.1616 gram H_2O.

	Calculated for $(C_{10}H_{14}NO)_3CHCl_3 + 2H_2O$.	Found.
C	52.85	53.33
H	7.40	7.39

Succinylcamphoroxime, $C_{10}H_{14}NOOCCH_2CH_2COOH$.—Camphoroxime, in ether solution, was treated with succinic anhydride on a water-bath with reflux condenser and with constant stirring, for twenty-four hours. On removing the ether a heavy colorless and almost inodorous oil remained. Excess of the anhydride was removed by redissolving in a small quantity of ether, filtering, and treating with an excess of warm water. Boiling with water or treating with alkalies breaks it up into the oxime and succinic acid. The oil thus purified appeared quite stable, boiling at 246°, with decomposition. On standing over sulphuric acid for several weeks the substance began to decompose, changing from a colorless oil to a substance looking like glue. Two analyses gave the following numbers :

I. 0.1915 gram of the substance gave 0.4460 gram CO_2, and 0.1540 gram H_2O.

II. 0.1624 gram of the substance gave 0.3761 gram CO_2, and 0.1186 gram H_2O.

	Calculated for $C_{10}H_{14}NOOCCH_2CH_2COOH$.	Found. I.	Found. II.
C	62.92	63.51	63.15
H	7.86	8.91	8.17

CAMPHOROXIME DERIVATIVES.

By G. B. Frankforter and P. M. Glasoe.

As already stated, camphoroxime, treated with certain acid anhydrides, forms esters of the respective acids. In some cases the reaction took place with greater or less difficulty, while in others the ester was readily formed together with a small quantity of the camphor nitril.

Phthalylcamphoroxime, $C_{10}H_{16}NOOCC_6H_4COOH$.—Camphoroxime remains unchanged if heated for several hours with phthalic anhydride in an ether solution. If, however, benzene or toluene is substituted for ether and the substances heated for several hours in one of these solvents with an excess of the anhydride, a reaction takes place, forming the ester, a part of which crystallizes out if a limited amount of the solvent is used. The ester thus formed contained some free phthalic anhydride, which was partly removed by redissolving in benzene and the last trace removed by heating with water. The substance thus purified melted at 135°.5, decomposing at that temperature and liberating phthalic acid and the nitril. It is soluble in ether, alcohol, and chloroform, and readily so in benzene. It is insoluble in carbon disulphide. It crystallizes from dilute alcohol in fine, white needles. Sodium hydroxide readily breaks it up into the oxime and phthalic acid. Various attempts to isolate the sodium salt failed. Heated in boiling alcohol, it slowly changes to the camphor nitril and phthalic acid. At the same time a small quantity of a colorless, inodorous oil was obtained which, although not analyzed, was, in all probability, an ethyl ester of the phthalyloxime. An analysis of the purified crystals gave the following results:

0.1322 gram of the dried substance gave 0.3319 gram CO_2, and 0.0851 gram H_2O.

	Calculated for $C_{10}H_{16}NOOCC_6H_4COOH$.	Found.
C	68.57	68.47
H	6.66	7.14

The Action of Formaldehyde on Camphoroxime.

Camphorformaldoxime, $C_{10}H_{18}NOCH_2OH+H_2O$.—Camphoroxime remains apparently unchanged when treated with formaldehyde in the cold, but when heated on a water-bath with a reflux condenser for several hours, fresh aldehyde being added from time to time, the oxime changes to an oil with the odor both of aldehyde and the oxime. On standing for some time in the air it changes into a solid mass, still holding, however, some free aldehyde. An attempt to analyze both the oil and the solid substance failed, as results were obtained varying all the way from 1 to 3 molecules of the aldehyde to one of the oxime.

The oil was then placed in a large quantity of water and allowed to remain for several days, when beautiful, large, white crystals appeared. These crystals were filtered off and examined. The substance no longer contained free aldehyde. It melted at 62° to 63°. It proved to be comparatively stable, being readily recrystallized out of water in large flakes. If boiled, however, for some time, in water, it breaks down into the oxime and aldehyde. Strong acids also break it down into the same substances. It contains 1 molecule of water of crystallization, which can be removed by heating for some time at a temperature of 50°, or by drying over sulphuric acid for several hours.

0.3542 gram of the substance, dried to constant weight over sulphuric acid, lost 0.1105 gram.

	Calculated for $C_{10}H_{18}NOCH_2OH + H_2O$.	Found.
H_2O	8.37	8.2

Analysis of the substance dried over sulphuric acid gave the following numbers:

I. 0.1811 gram of the substance gave 0.4402 gram CO_2, and 0.1667 gram H_2O.

II. 0.2345 gram of the substance gave 0.5799 gram CO_2, and 0.2042 gram H_2O.

III. 0.1913 gram of the substance gave 13.2 cc. of N at 739 mm. pressure and 23°.

	Calculated for $C_{10}H_{16}NOCH_2OH$.	Found. I.	II.	III.
C	67.00	67.04	67.44	....
H	9.64	10.10	9.68	....
N	7.10	....	....	7.6

Great difficulty was experienced in obtaining the large, flaky crystals. Sometimes they formed readily, while at other times it was next to impossible to obtain them. It was found necessary to heat the oxime a definite length of time with slight excess of the aldehyde. The oxime thus heated for eight hours on a water-bath completely changed to the oil. Heated longer than that time, the tendency to form the nitril was apparent; at the same time camphoroxime was formed.

Camphorparaformaldoxime, $C_{10}H_{16}N(C_2H_4O_2)$.—As stated above, camphoroxime, treated with formaldehyde, dissolves, and forms an oil which gave variable results on analysis, but from which the formyl compound was obtained. If, however, the oxime is heated with an excess of the aldehyde and allowed to stand in a warm place and in the direct rays of the sun, a thick oily substance is formed which floats on the aldehyde. This oil was separated by extracting with ether, and then examined. The oil, purified by extraction with ether, had the odor of camphor, and, at the same time, that of formaldehyde. If kept over sulphuric acid for several days, it breaks down into camphoroxime and the aldehyde. The decomposition does not take place if the substance is kept cold. Dropped into water containing a little formaldehyde, it changes readily into the formyl compound, as indicated by the form of crystal, and by the melting-point. At the same time another substance was formed which remained in the aldehyde solution and which was identified as paraformaldehyde. Analysis of the oil which had been purified from ether gave the following results:

I. 0.2060 gram of the oil gave 0.4918 gram CO_2, and 0.1688 gram H_2O.

II. 0.2265 gram of the oil gave 0.5398 gram of CO_2, and 0.1896 gram H_2O.

	Calculated for $C_{10}H_{16}N(C_2H_4O_2)$.	Found. I.	II.
C	65.27	65.10	64.99
H	8.78	9.10	9.3

The Action of Sulphothionyl Chloride on Camphoroxime.

Sulphothionyl chloride acts violently on camphoroxime, undoubtedly forming with it several different compounds. If, however, the chloride be diluted with ether, the reaction is less violent, and a monochlor derivative of camphoroxime is formed. This substance, when first obtained, showed the presence of sulphur, but an analysis[1] revealed only a mere trace which was afterwards removed by recrystallization. Several attempts to obtain the sulpho compound failed, although indications of such a substance were observed on treating the oxime with the liquid chloride alone.

Monochlorcamphoroxime, $C_{10}H_{14}ClNOH$. — Camphoroxime was dissolved in ether and sulphothionyl chloride cautiously added. A reaction began immediately and a fine, amorphous powder was precipitated. If the chloride is diluted with ether and added drop by drop, the substance appears as fine needle-shaped crystals. So perfectly insoluble was the substance in ether that the reaction was quantitative. Two grams of the oxime dissolved in 50 cc. of ether and an excess of the chloride added, gave 2.3 grams of the chloride. The substance thus obtained was a fine, white, crystalline powder, readily soluble in methyl and ethyl alcohols and water. The substance was purified by dissolving in a small quantity of alcohol and precipitated by adding ether. Thus precipitated and dried, the substance melted at 290° C. It contained no water of crystallization. Analyses of the dried substance gave the following results:

I. 0.1737 gram of the dried substance gave 0.3860 gram CO_2, and 0.1494 gram H_2O.

II. 0.1148 gram of the dried substance gave 0.2560 gram CO_2, and 0.0872 gram H_2O.

III. 0.1188 gram of the dried substance gave 0.08756 gram AgCl.

IV. 0.1133 gram of the dried substance gave 0.07985 gram AgCl.

[1] 0.4100 gram of the chloride gave 0.0076 gram of $BaSO_4$.

	Calculated for $C_{10}H_{13}ClNOH$.	Found. I.	II.	III.	IV.
C	59.55	60.6	60.81	....	....
H	7.94	8.55	8.43	....	....
Cl	17.63	....	....	17.48	18.29

Up to the present nothing has been determined concerning the position of the chlorine. Several isomeric forms are possible. The chlorine has been removed, both by silver oxide and by sodium hydroxide, and the products are now under examination.

THE LABORATORY PRODUCTION OF ASPHALTS FROM ANIMAL AND VEGETABLE MATERIALS.[1]

By Wm. C. Day.

By carrying out operations of distillation at the ordinary atmospheric pressure upon animal and vegetable matter, both separately and mixed, I have succeeded during the past year in producing three different materials, all of which present in different degrees the properties characteristic of asphalts. Two of these materials quite closely resemble asphalts occurring in nature; *viz.*, gilsonite and elaterite as found in Utah.

Postponing for the present a consideration of the reasons which led to these experiments, I will first give a description of the work done and a statement of the results obtained since the publication, last summer, of a preliminary paper[2] on the same subject.

The first experiment was to distil from an iron retort a mixture of fresh fish (herring from the Delaware) and fat pine wood partly in the form of sawdust and partly in sticks. The retort was connected with a short glass tube by means of a joint of plaster of Paris and asbestos; this tube was connected at the other end by a similar joint with a small iron gas pipe four feet long, placed upon a combustion furnace by which it could be maintained at a red heat. The retort was heated by gas furnaces and the distillation was carried to complete carbonization of the organic matter. An ordinary Liebig's

[1] Published by permission of the U. S. Geological Survey. Read at the stated meeting of the Chemical Section of the Franklin Institute, Feb. 21, 1899.

[2] Proc. Amer. Phil. Soc., 37, 171.

condenser served to condense the mixed oil and water as it issued from the red hot gas pipe. The distillation-product consisted of water of a yellowish-red color, and a dark, nearly black, mobile oil which for the greater part floated upon the water, although toward the close of the distillation a little oil would usually sink through the water.

Twelve operations of distillation consumed 9,882 grams of wood and 8,170 grams of fish and yielded 3,010 cc. oil of sp. gr. 0.9837 and 8,240 cc. water. The average distillation shows, therefore, the figures 823.5 grams wood, 680.8 grams fish, 250.8 cc. oil, and 686.7 cc. water. These average figures were approximated in each single distillation.

The oil was separated from the water and then dried by standing over chloride of calcium. A combustion of this oil, using copper oxide and lead chromate, gave the following results:

0.3104 gram oil gave 0.9593 gram CO_2; and 0.2794 gram H_2O, or carbon 84.28 per cent, and hydrogen 10 per cent.

The dried oil was then subjected to distillation by itself in a hard glass retort provided with a thermometer. A few drops of oil accompanied by a little moisture came over at 80° C.; the temperature rose rapidly to 120°, at which point distillation proceeded rapidly, giving a distillate lemon-yellow in color and slightly turbid from moisture. The receiver was changed at 180°, when the distillate appeared darker in color but free from moisture. The receiver was changed at 245°, 315°, and 340°, at which last point the thermometer was removed; after this the distillation was conducted to about 425°, as nearly as could be judged by the rate at which the temperature had been rising. At 315° a greenish fluorescence appeared. When the boiling was stopped the contents of the retort consisted of a mobile, homogeneous, black liquid containing no solid particles of any kind. When the retort cooled, this oil solidified to a black, shining mass, showing conchoidal fracture, brittle, and pulverizing to a brownish-colored powder slightly darker than the powder of Utah gilsonite, which it closely resembled; in fact it was only by the rounded surface of the artificial product that the two could be distinguished by inspection. A number of distilla-

tions were made with essentially the same experience as just described, except that the material obtained the first time was slightly sticky to the touch and entirely soluble in carbon bisulphide, while the samples obtained subsequently were not at all sticky, and were not entirely soluble in the bisulphide.

Subjected to combustion, the sample resulting from the first distillation gave the following result:

0.2211 gram substance gave 0.7100 gram CO_2; and 0.1540 gram H_2O; or carbon 87.57 per cent, hydrogen 7.74 per cent.

Two combustions of the artificial gilsonite, finally made in quantity, gave the following results:

I. 0.2529 gram substance gave 0.8031 gram CO_2, and 0.1599 gram H_2O.

II. 0.3015 gram substance gave 0.9564 gram CO_2, and 0.1938 gram H_2O.

	I.	II.
Carbon	86.61	86.51
Hydrogen	7.02	7.10

Two nitrogen determinations by Kjeldahl's method, using in the first case 1.1990 grams substance, and in the second 0.9824, gave nitrogen 1.95 and 1.86 per cent, respectively.

Two determinations of sulphur by Peckham's method[1] resulted as follows:

I. 2.0218 grams substance gave 0.0136 gram $BaSO_4$.

II. 1.9988 grams substance gave 0.0114 gram $BaSO_4$.

	I.	II.
S	0.092	0.078

According to the figures obtained the composition of the artificial gilsonite appears to be as below. For the sake of comparison, the figures for natural Utah gilsonite are also given here as well as elsewhere.

	Artificial.		Natural.
Carbon	86.56		85.83
Hydrogen	7.06		10.59
Nitrogen	1.91		2.59
Sulphur	0.08		0.26
Oxygen (by diff)	4.39		0.63
		Ash	0.10
	100.00		100.00

[1] Jour. Soc. Chem. Ind., 16, No. 12, 1897.

While the differences in composition between these two materials are not great, still they can by no means be regarded as insignificant, particularly as regards the hydrogen and oxygen. It is true, however, that much greater differences between two natural asphalts taken from sources in the same neighborhood have been found.

Determinations of solubility in the following solvents were made: Carbon bisulphide, turpentine, ether, gasoline, and absolute alcohol. The method employed was to treat a weighed portion of the substance with the solvent until no further action took place, and then weigh the undissolved residue on a tared filter.

Carbon Bisulphide.

I.

	Weight.
Substance taken	0.5505
Undissolved residue	0.1060
Dissolved substance	0.4445

Per cent soluble in CS_2 = 80.74.

II.

	Weight.
Substance taken	0.6970
Undissolved residue	0.1293
Dissolved substance	0.5677

Per cent soluble in CS_2 = 81.44.

Turpentine.

	Weight.
Substance taken	0.9041
Undissolved residue	0.4568
Dissolved substance	0.4473

Per cent soluble in turpentine = 49.47.

Ether.

	Weight.
Substance taken	0.5776
Undissolved residue	0.1904
Substance dissolved,	0.3872

Per cent soluble in ether = 67.03.

Gasoline.

	Weight.
Substance taken	0.5339
Undissolved residue	0.2845
Substance dissolved	0.2494

Per cent soluble in gasoline = 46.71.

Absolute Alcohol.

	Weight.
Substance taken	0.5547
Undissolved residue	0.2862
Substance dissolved	0.2685

Per cent soluble in alcohol = 48.40.

All the solutions obtained were characterized by a more or less marked greenish fluorescence, which is also true of the natural gilsonite.

	Action of solvents.	
Solvent.	Utah gilsonite.	Artificial gilsonite.
Carbon bisulphide	99.50 { First product	100.00
	{ Second "	81.44
Turpentine	97.34	49.47
Ether	73.08	67.03
Gasoline	63.08	46.71
Alcohol	34.81	48.40

While the above table shows in some cases quite notable differences in solubility, every one of the solvents exercises in each case a pronounced effect, all figures being above 30 per cent and generally nearly 50 per cent or more.

The action of concentrated nitric acid upon the natural and the artificial material is peculiar, and of exactly the same character. This action consists in completely dissolving the material with copious evolution of brown fumes and the production of a dark-red solution, which, when diluted with water, yields a flocculent precipitate much resembling freshly precipitated ferric hydroxide.

In the course of an investigation of Utah gilsonite[1] carried out some years since, I separated from the oils distilled from the mineral certain basic compounds suggestive in odor of the

[1] Jour. Franklin Institute, 140, 221.

pyridine or quinoline series. These bodies were obtained by the extractive action of dilute sulphuric acid upon the oils. From such solution they are thrown down by alkalies as flocculent precipitates.

The same kind of substances were obtained from the oil which by distillation yielded the artificial gilsonite. The method of treatment adopted to extract these basic substances was to shake the oil with dilute sulphuric acid, and then pass steam into the mixture contained in a large flask until oil no longer distilled off with steam. On neutralizing the residual acid with caustic soda solution a precipitate, looking and smelling like that from gilsonite oil, was obtained. The precipitate was alternately redissolved in sulphuric acid and reprecipitated by alkali a number of times and then, after washing with water, was left on a filter to dry. On drying, however, the material largely disappeared, thus showing its volatility, which the solid appearance, when freshly precipitated, had failed to suggest. It is evident, however, that the presence of these basic compounds affords another element of similarity between the natural and the artificial product, and also between these bodies and California petroleum.

Distillation of Fish Alone.

The interesting character of the product obtained by distilling a mixture of fish and wood, and the similarity between this and Utah gilsonite suggested the advisability of carrying out the same kind of experiments with fish alone, and also with wood alone. Accordingly, a number of charges of the same kind of fish was distilled, using the same apparatus as was employed for the mixture of wood and fish.

In all 4,585 grams of fish were distilled, yielding 700 cc. of oil and 2,830 cc. water. The distillate consisted of a yellow emulsion difficult to break up; the distillate from the fish and wood mixed gave no emulsion at all, but presented a well-defined line of separation between the oil and water. The emulsion was separated into oil and water by heating upon the water-bath, the oil being eventually brought to the surface of the water. Much ammonia was produced during the distillation.

An attempt was made to dry the oil by allowing it to stand over chloride of calcium for a number of days, but it could not be perfectly dried in this way. Success in drying was finally attained only by aspirating a current of dry air through the oil while it was heated upon the water-bath.

On attempting to distil the fish oil from a retort as was done with the oil from the mixture of fish and wood, such vigorous and explosive "bumping" followed as to carry the contents of the retort over mechanically so that it was found impossible to distil it in this way. The appearance of moisture during this attempt to distil an oil which had been thoroughly dried made it evident that the water was formed during the distillation. The oil was transferred from the retort to an iron crucible and heated cautiously until the stage of water formation was passed, and then heated more strongly. After heating for a time, the contents of the crucible were allowed to cool, when a very sticky, thick, semiliquid mass remained. It looked and smelled more like a maltha from Montana that I had examined a few years since, than anything else I could compare it to. The material was again heated in the crucible, it being allowed to boil freely ; on cooling again a solid was obtained, black in color and elastic, so that if bent nearly double it would fly back to its original shape like a thick piece of India rubber. It could be easily cut but not pulverized, although if struck a blow with a hammer it would break with conchoidal fracture.

Determinations of carbon, hydrogen and nitrogen were made with the following results:

I. 0.2366 gram substance gave 0.6638 gram CO_2, and 0.1933 gram H_2O.

II. 0.2333 gram substance gave 0.6618 gram CO_2, and 0.1916 gram H_2O.

III. 0.5233 gram substance gave by Kjeldahl's method ammonia corresponding to 4.19 per cent of nitrogen.

IV. 0. 8896 gram substance gave ammonia corresponding to 4.27 per cent nitrogen.

V. 2.0402 grams substance gave 0.0287 gram $BaSO_4$.

VI. 1.9954 grams substance gave 0.0276 gram $BaSO_4$.

	I.	II.	III.	IV.	V.	VI.
Carbon	76.51	77.36	....	....	....	....
Hydrogen	9.08	9.12	....	....	....	....
Nitrogen	....	....	4.19	4.27	....	....
Sulphur	....	....	....	....	0.19	0.19

This material, if cooled down, became harder and less susceptible of bending; the same kind of change seemed to result also as the material became older, as after some months it became harder and more brittle.

The following analytical results were obtained upon a sample of elaterite from Utah. This material, in lump form, was hard and not at all capable of being bent; it was, however, quite flexible when sawed into thin slabs. The percentages of carbon and hydrogen found are not far from those of the asphalt from fish alone.

I. 0.2993 gram substance gave 0.8024 gram CO_2, and 0.2550 gram H_2O.

II. 0.1995 gram substance gave 0.5404 gram CO_2, and 0.1698 gram H_2O.

	I.	II.
Carbon	73.11	73.88
Hydrogen	9.46	9.45

Further investigation of this material is now being carried out. According to Dana's Mineralogy, p. 734, elaterite, analyzed by Johnston, contains 84 to 86 per cent carbon, and 12.3 to 13.2 per cent hydrogen. I am unable to give the authority for calling the Utah material elaterite, but in composition it evidently resembles much more nearly the material obtained from fish than it does the elaterite described by Dana. The much lower percentage of carbon than is contained in gilsonite is noteworthy.

Treatment of oil obtained from fish alone with dilute sulphuric acid gave a solution of basic nitrogen compounds which could be precipitated by alkalies just as in the case of oil from natural or artificial gilsonite. The odor of these basic substances was of the same character, whatever the source.

The following determinations of the solubility of the asphalt from fish alone were made:

Carbon Bisulphide.

	Weight.
Substance used	0.2999
Substance undissolved	0.0954
Substance dissolved	0.2045

Per cent soluble in CS_2 = 68.19.

Turpentine.

	Weight.
Substance used	0.3163
Substance undissolved	0.1665
Substance dissolved	0.1498

Per cent soluble in turpentine = 47.36.

Ether.

	Weight.
Substance used	0.2662
Substance undissolved	0.1087
Substance dissolved	0.1575

Per cent soluble in ether = 59.17.

Gasoline.

	Weight.
Substance used	0.3733
Substance undissolved	0.2419
Substance dissolved	0.1314

Per cent soluble in gasoline = 35.19.

Absolute Alcohol.

	Weight.
Substance used	0.4239
Substance undissolved	0.2074
Substance dissolved	0.2165

Per cent soluble in alcohol = 51.07.

Distillation of Wood Alone.

The same kind of rich and heavy pine as was used in mixture with fish was subjected to distillation by itself. In all 4,588 grams were used, yielding 1,150 cc. of oil and 890 cc. water.

It is interesting to note here the much larger proportion of oil obtained than resulted from the distillation of fish alone. The distillation was accompanied by the production of a thick, white smoke which could not be condensed. The distillate was strongly acid. The oil, after drying, showed a specific gravity of 0.992. It was subjected to distillation by itself, the same fractions being collected, as in the case of the distillation of oil from wood and fish. The first fraction, 90°–145°, was light-yellow in color and slightly turbid from moisture; the second, 145°–180°, was darker yellow; the third, 180°–245°, was greenish-black; the last one showed green fluorescence. After distilling off somewhat more than half the oil the black but perfectly mobile liquid was allowed to cool, when it solidified to a black, shining mass, very brittle, and showing conchoidal fracture. While the general color was black, inspection of a thin edge along a line of fracture showed a purple color such as could not be seen with the material from wood and fish. The specific gravity was found to be 1.0825. When pulverized the powder, in the course of several days, would cement together and re-form a hard, rigid mass.

Determinations of carbon, hydrogen, and nitrogen gave the following results:

I. 0.2078 gram substance gave 0.6568 gram CO_2, and 0.1549 gram H_2O.

II. 0.9362 gram substance gave ammonia corresponding to 0.26 per cent nitrogen.

III. 0.8884 gram substance gave ammonia corresponding to 0.33 per cent nitrogen.

Determinations of sulphur gave only traces.

	I.	II.	III.
Carbon	86.20	....	....
Hydrogen	8.28	....	....
Nitrogen	....	0.26	0.33

The following determinations of solubility were made:

Carbon Bisulphide.

I.

	Weight.
Substance used	0.3604
Substance undissolved	0.0050
Substance dissolved	0.3554

Per cent soluble in CS_2 = 98.61.

II.

Substance used	0.3868
Substance undissolved	0.0003
Substance dissolved	0.3865

Per cent soluble in CS_2 = 99.92.

Turpentine.

I.

	Weight.
Substance used	0.4498
Substance undissolved	0.0155
Substance dissolved	0.4343

Per cent soluble in turpentine = 96.55.

II.

Substance used	0.4218
Substance undissolved	0.0167
Substance dissolved	0.4051

Per cent soluble in turpentine = 96.04.

Ether.

I.

	Weight.
Substance used	0.3589
Substance undissolved	0.0153
Substance dissolved	0.3436

Per cent soluble in ether = 95.45.

II.

Substance used	0.4084
Substance undissolved	0.0130
Substance dissolved	0.3954

Per cent soluble in ether = 96.81.

Gasoline.

I.

	Weight.
Substance used	0.5342
Substance undissolved	0.0441
Substance dissolved	0.4901

Per cent soluble in gasoline 91.74.

II.

Substance used	0.3582
Substance undissolved	0.0412
Substance dissolved	0.3170

Per cent soluble in gasoline = 88.49.

Alcohol.

	Weight.
Substance used	0.5548
Substance undissolved	0.2130
Substance dissolved	0.3418

Per cent soluble in alcohol = 61.60.

High solubility is characteristic of this material in all cases.

A quantity of the oil from wood alone was treated with dilute sulphuric acid for the purpose of testing for basic oils. No trace of these oils could be precipitated, however, by neutralizing the acid with sodium hydroxide.

In connection with the present investigation a complete analysis of Utah gilsonite has been made with results that are somewhat lower in carbon and in sulphur than those obtained and published a few years since.[1] Instead of using finely powdered lead chromate, together with copper oxide, as in the first analysis, a large quantity of coarse granules of lead chromate were employed with results that showed better agreement.

In this connection it should be remarked that the use of copper oxide in combustions of hydrocarbons has not infrequently given trouble in the form of irregularities in the figures for carbon. Professor Peckham, in a recent conversation,

[1] Jour. Franklin Inst., 140, 221.

called my attention to a remark made to him by Warren to the effect that copper forms carbides which are oxidized with difficulty, and hence, according as these are formed or oxidized in succeeding combustions, the figures for carbon will vary. This point is now being investigated. Certain it is, however, that asphalts are troublesome substances in elementary analysis. This statement is thoroughly borne out by a study of the literature of these bodies.

The following are the results of analysis of Utah gilsonite.

I. 0.2738 gram substance gave 0.2603 gram H_2O, and 0.8631 gram CO_2.

II. 0.2017 gram substance gave 0.1930 gram H_2O, and 0.6336 gram CO_2.

III. 1.0347 grams substance gave ammonia, by Kjeldahl's method, corresponding to 2.65 per cent nitrogen.

IV. 0.9363 gram substance gave ammonia corresponding to 2.53 per cent nitrogen.

V. 2.1651 grams substance gave 0.0390 gram $BaSO_4$.

VI. 2.0017 grams substance gave 0.0388 gram $BaSO_4$.

	I.	II.	III.	IV.	V.	VI.
Carbon	85.98	85.67	....	....	....	....
Hydrogen	10.56	10.62	....	....	....	....
Nitrogen	....	....	2.65	2.53	....	....
Sulphur	....	....	....	....	0.25	0.27

Taking the averages of these results, the percentage composition appears to be:

Carbon	85.83
Hydrogen	10.59
Nitrogen	2.59
Sulphur	0.26
Oxygen (by diff.)	0.63
Ash[1]	0.10
	100.00

[1] Quoted from paper on gilsonite: Jour. Frank. Inst., **140**, 221.

Table Giving Analytical Results.

Name of substance.	Carbon.	Hydrogen.	Nitrogen.	Sulphur.	Oxygen.	Ash.
Oil from fish and wood	84.28	10.00	not determined			none
Artificial gilsonite fr. first preparation	87.57	7.74	"	"		"
Artificial gilsonite made finally	86.56	7.06	1.91	0.08	4.39	"
Utah gilsonite	85.83	10.59	2.59	0.26	0.63	0.10
Asphalt fr. fish alone	76.93	9.10	4.18	0.19	9.60	none
Utah elaterite	73.11	9.45	1.90	3.17	12.37	trace
Asphalt fr. wood alone	86.20	8.28	0.29	trace	5.23	none
Utah nigrite	83.33	8.69		0.42		0.12

	Fixed carbon.	Volatile matter.	Ash.
Utah nigrite	36.33	63.55	0.12

The specific gravities of various substances determined in the course of the present investigation are given in the following table :

Specific Gravities.

Oil obtained from primary distillation of fish and wood, temperature 26° C.	0.9837
First fraction of above oil 80°–145° C. when distilled by itself, temperature 25.8° C.	0.842
Last fraction in same distillation 340° C., temperature 25.9° C.	1.002
Utah gilsonite, temperature 26° C.	1.0354
Artificial gilsonite, temperature 26° C.	1.1713
Asphalt obtained from wood alone, temperature 26° C.	1.0825
Asphalt obtained from fish alone, temperature 26° C.	1.0590
Oil from wood and fish volatile with steam, temperature 26° C.	0.8940
Oil obtained in primary distillation of wood, temperature 26.4° C.	0.9920

TABLE OF SOLUBILITIES IN VARIOUS SOLVENTS.

Name of substance.	Carbon bisulphide all.[1]	Turpentine.	Ether.	Gasoline.	Absolute alcohol.
Artificial gilsonite	81.09	49.47	67.03	46.71	48.40
Utah gilsonite	99.50	97.34	73.08	63.08	34.81
Asphalt fr. fish alone	68.19	47.36	59.17	35.19	51.07
Asphalt fr. wood alone	99.26	96.29	96.13	90.12	61.60

[1] This determination involved no weighings, as when the solution was filtered, nothing insoluble remained on the filter.

The foregoing experiments suggested themselves as the result of a number of years of experimental work upon asphalts from a number of natural sources in the western part of the United States, and a study of the literature of natural hydrocarbons, solid, liquid, and gaseous, and the synthetical experiments which have been carried out by Warren, Engler, and Sadtler. From the chemical-geological standpoint the writings of Peckham have been very suggestive, advocating as they have done, the idea that bitumens are distillates together with water of organic matter which has accumulated in strata of all ages in the earth.

Utah gilsonite is the natural material to which the writer has given most experimental study. This mineral contains very little oxygen and sulphur, almost no ash, but a notable quantity of nitrogen which shows itself in distillation-products in the form of basic substances similar in a general way to the pyridine and quinoline series, and of the same character as the basic substances obtained by Peckham and Salathé from California petroleum, and freely commented upon by Peckham in a number of papers by him.

These nitrogen compounds suggest that the bodies containing them are of animal origin. It seemed, however, to the writer that a material of exclusively animal origin would be likely to contain a larger proportion of oxygen than is contained in such material as natural gilsonite, and that in laboratory experiments to reproduce asphalts low in oxygen, vegetable material should be present at the same time, and that opportunity should be afforded for the oxygen containing distillates from oils and animal substances to react at a fairly high temperature with the abundant gaseous hydrocarbons produced by distilling wood or, in general, vegetable material. The result of such reaction between bodies of the nature just described would be to eliminate oxygen from the oily distillate by causing it to form water and carbon dioxide with the hydrogen and carbon of gaseous hydrocarbons. This idea was confirmed by the fact that in his experiments to produce petroleum-like substances and paraffin from linseed oil Sadtler[1] noticed the odor of acrolein and referred to it as follows :

[1] Proc. Amer. Phil. Soc., 36, 93.

"At first the odor of acrolein was very pronounced and powerful, showing that the glycerine of the glycerides composing the oil was being decomposed; later the odor was more that of a cracked petroleum oil, showing that the linoleic and other acids of the oil were undergoing decomposition." On another page the same writer says, "Of course the fractions must be obtained on a sufficiently large scale to admit of thorough purifying before the character of the hydrocarbons can be studied. At present they contain impurities such as aldehyde-like and possibly ketone products. They reduce ammoniacal silver solutions and indicate thus the presence of these impurities."

The following facts based upon a consideration of the character of the distillates obtained from the mixed animal and vegetable matter, from the fish alone, and from the wood alone tend to show the correctness of the writer's position in an attempt to produce an asphalt low in oxygen. The table of ultimate analyses given below shows that there is less than half as much oxygen in the asphalt from wood and fish mixed as in that from fish alone.

Ultimate Analyses.

	Ash.	Carbon.	Hydrogen.	Sulphur.	Nitrogen.	Oxygen.
Utah gilsonite	0.10	85.83	10.59	0.26	2.59	0.63
Utah elaterite	....	73.49	9.46	3.17	1.90	12.37
Artificial gilsonite fr. wood and fish	....	86.56	7.06	0.08	1.91	4.39
Asphalt from wood	....	86.20	8.28	trace	0.29	5.23
Asphalt from fish	....	76.93	9.10	0.19	4.23	9.55

The following table giving the yields of water and oil in the various distillations is also of interest as showing the effect of water-forming reactions between hydrocarbons and oxygen compounds which doubtless took place in the hot tube through which the vapors were passed before condensation.

Material used.		Oil produced.	Water produced.
Wood. Grams.	Fish. Grams.	cc.	cc.
9882	8170	3010	8240
....	4585	700	2830
4588	....	1150	890

If the wood and fish when distilled together had yielded oil and water in the same proportion as when each was distilled by itself, then there should have been a yield of 3724 cc. of oil from the mixture instead of the 3010cc. actually produced, and instead of 8240 cc. of water there should have been only 7321 cc.

The question of the origin of asphalts is one that cannot be intelligently discussed apart from that of the origin of petroleum, or, more broadly still, apart from the origin of the bitumens in general which include natural hydrocarbons in all states of matter: solid, liquid, and gaseous. Of these three states liquid petroleum has for a variety of obvious reasons received the most attention scientifically and technologically.

The connection quite generally believed at present to exist between petroleum and the asphalts is expressed in Dana's Mineralogy, p. 751, as follows: "The more solid kinds graduate into the pittasphalts or mineral tar, and through these there is a gradation to petroleum. The fluid kinds change into the solid by the loss of a vaporizable portion on exposure, and also by a process of oxidation which consists first in a loss of hydrogen and finally in the oxygenation of a portion of the mass."

If it be accepted as true that petroleum and the asphalts are related, as the quotation just made would indicate, then it follows, of course, that any view as to the origin of petroleum also applies to the asphalts. A study of the literature concerning theories as to the origin of petroleum reveals a number which differ fundamentally from each other, and which are based largely upon geological evidence. It does not seem necessary here to give detailed consideration to these hypotheses in view of the thorough manner in which they have been recently summed up and reviewed by Myers, Sadtler, Peckham, Mabery, Phillips, and D. T. Day in a series of papers[1] read before the American Philosophical Society, February 5th, 1897. The comprehensive résumé given by Boverton Redwood in his work on Petroleum also contributes to make further detailed review superfluous at this time. It seems,

[1] Proc. Amer. Phil. Soc., **36**, 93.

however, that the propriety of attempting to make any one of these theories cover the entire problem of the origin of petroleum is very questionable in view of the fundamental differences in character and properties between petroleums of different sources which by the work of Schorlemmer, Warren, Mabery, Beilstein and Kurbatow, Markownikoff, Schützenberger and Jonine, Zaloziecky, and others, have been shown to exist. The following quotation from Boverton Redwood's work is of interest in this connection :

Referring to his résumé of theories he says, " From the account given in this section, it will be seen that there has been an abundance of speculation as to the origin of bitumen and that, in regard to some of the theories, a considerable amount of experimental proof has been forthcoming. Probably, on the whole, the Höfer-Engler views at present have the largest number of adherents, and in respect, at any rate, to certain descriptions of petroleum, are the most worthy of acceptance. At the same time, a careful study of the subject leads to the conclusion that some petroleum is of vegetable origin, and it therefore follows that no theory is applicable in all cases."

When we consider, for example, the striking differences in character between California petroleum and Pennsylvania petroleum to which Peckham, in a number of different papers, has earnestly called attention, the force of the last sentence quoted from Redwood will undoubtedly be keenly appreciated. Commenting upon the Höfer-Engler theory, Prof. Peckham[1] says, " Dr. Engler therefore considers that some change in the animal remains must have taken place in the earth, whereby all nitrogenous and other matters, save fats, were removed, the petroleum being formed from this fat alone, by the combined action of pressure and heat or by pressure only.

" In summing up the evidence as to origin, Höfer expresses the belief that petroleum is of animal origin, and has been formed without the action of excessive heat, and observes that it is found in all strata in which animal remains have been discovered.

" Combining these two statements, we arrive at this conclu-

[1] Proc. Amer. Phil. Soc., 36, 106.

sion as the Höfer-Engler theory, that bitumens are of animal origin, formed at low temperatures from fats alone by the combined action of pressure and heat."

"Steam is left out of this formula, and it is therefore inadequate. There is no evidence whatever that any portion of the crust of the earth has ever been subjected to the combined action of heat and pressure without the presence of steam or hot water, and, in my judgment, the steam has been a very potent factor in determining not only the formation but the transference of bitumens."

The writer, from his experience in the production of asphalts, as already described in this paper, feels like endorsing most heartily the views of Peckham in regard to the necessity of steam as a factor in the production of such asphalts, at least, as have been made the subject of experimental study.

The following is a quotation from Professor Peckham's paper on "The Genesis of Bitumens as Related to Chemical Geology,"[1] which sums up the most important features of his views as to the genesis of bitumens. The laboratory results which I have so far obtained seem to be quite fully in accordance with the conclusions which Prof. Peckham has reached.

"Upon this hypothesis, that bitumens are distillates, all of the variations observed in bitumens of different geological ages are easily explained. The earliest forms of animal and vegetable life are admitted to have been nearly destitute of nitrogen; hence, when these forms accumulated in sediments which, borne down by deposits above them, invaded an isothermal that admitted of their distillation, they must have been distilled, in the presence of steam, at the lowest possible temperature; they must have been distilled under a gradually increasing pressure, the extent of which depended upon the porosity of sediments above them up to the surface. They must also have been distilled under a gradually increasing temperature which would have been largely controlled by the pressure. While the temperature and pressure would have in every instance been the least possible, with steam always present, these physical conditions would on account of the

[1] *Loc. cit.*

varying porosity and consequent varying resistance of the overlying mass, have produced very great effects in some instances and very slight effects in others. As a consequence, we have in natural bitumen, as in artificial distillates, materials varying in density from natural gas to solid asphaltum.

"If these distillates proceeded from materials that would yield paraffine, these permanent and stable compounds from marsh-gas to solid paraffine, remained in the receptacles that nature had provided for them until they were released by the drill. If, however, the distillates proceeded from sediments of a different geological age, containing animal and vegetable remains more highly organized, that would yield different series of hydrocarbons, with compounds of nitrogen, then a very different bitumen would be stored in these receptacles. Secondary reactions would convert these primary distillates into a great variety of substances.

"The contents of the original reservoirs borne down and invaded by heat might become involved in a second distillation at an increased pressure and temperature. Fractures of these reservoirs from excessive pressure might lead their contents to the surface along lines of contact of strata or with water containing sulphates by which an originally pure hydrocarbon would be converted into a sulphur bitumen. A nitro hydrocarbon, reaching the surface under these conditions, might by the combined action of evaporation and reaction with sulphates, pass through all the varying degrees of density from petroleum to maltha and become finally solid asphaltum, and this through the lapse of time and abundance of material on a scale of vast magnitude."

While it is true that most of the theories that have been advanced to explain the origin of bitumens have been directly concerned with the liquid variety ordinarily known as petroleum, and seem at least to have been based upon study, whether geological or chemical, of this variety to the exclusion of the solid form generally known as asphalt, still it is true that some theories have been advanced to explain directly the formation of asphalts aside from and independently of their possible relation to liquid petroleums.

Thus the Trinidad asphalt was looked upon by Wall[1] as having resulted from the gradual decomposition of vegetable matter found imbedded in it. This view is, however, no more tenable than the idea that the material originated from animal remains which have been found clearly indicated from a study of the composition of the asphalt.

When we consider the amount and the character of the strictly chemical work that has been done upon the asphalts or solid bitumens, it must be admitted that they have been decidedly neglected as compared with the liquid form. Even elementary analyses are in many cases unreliable, and there is much need of painstaking and persistent study in this field.

When we contemplate the marked differences between bitumens from different sources, it hardly seems reasonable to believe that any one theory as to the origin of these bodies can cover all the actual occurrences. It would seem that heat and pressure, singly and combined, and of various intensities acting with water both as liquid and as steam upon the same fundamental material, whether animal or vegetable, should produce a variety of carbonaceous substances differing from each other quite profoundly in physical and chemical properties. Again, similar or identical conditions prevailing with different kinds of material, whether animal or vegetable or mixtures of the two, should also yield products of various kinds. When, therefore, we consider the great possibilities of variation in combinations of natural forces, and also equally great possibilities of variation in the nature of the organic material upon which these forces may act, it is not surprising that we find as we do in various parts of the earth complicated and intimate carbonaceous mixtures, gaseous, liquid, and solid, which are usually summed up under the general name, bitumens.

The facts and figures given in this communication speak for themselves. Summed up they show that three asphaltic substances have been obtained by operations of distillation, primarily in presence of steam from natural animal and vegetable material, both separately and combined. The material obtained from the mixture of fish and wood, and called artificial

[1] Q. J. G. Soc., 16, 460.

gilsonite, so closely resembles the gilsonite from Utah that it is impossible, by inspection, to tell the two materials apart. The material obtained from fish alone also resembles what has been called (with questionable propriety) elaterite from Utah. While these two pairs of substances differ from each other to a greater or less extent in respect to the various parallel treatments to which they have been subjected, and while they also differ somewhat in chemical composition, as well as in solubility, specific gravity, streak, etc., these differences are all *in degree* and not in any single case *in kind*.

I am now engaged in the study of an asphalt known as nigrite, which occurs near the gilsonite of Utah. The differences between these two bitumens are throughout more striking than any that I have observed between the natural and the artificial substances treated of in this paper.

In conclusion, I take pleasure in acknowledging the benefit and the satisfaction I have derived from a study of the papers published by Professor Peckham, particularly the two entitled, "The Genesis of Bitumens as Related to Chemical Geology,"[1] and "On the Nature and Origin of Petroleum."[2]

I am indebted to my assistant, Mr. Eugene Leamy, for able cooperation throughout the entire work, and to one of my former pupils, Miss Georgia Porter, for the nitrogen determinations.

SWARTHMORE COLLEGE, PA.,
February 18, 1899.

Contributions from the Chemical Laboratories of the Massachusetts Institute of Technology.

XXII.—THE COMPOSITION OF NITROGEN IODIDE AND THE ACTION OF IODINE ON THE FATTY AMINES.

BY JAMES F. NORRIS AND ARTHUR I. FRANKLIN.

The action of the halogens on the fatty amines has been investigated by Wurtz,[3] Raschig,[4] Séliwanow,[5] and others. In all cases aqueous or alkaline solutions were used and the products obtained had the composition represented by the

[1] Proc. Amer. Phil. Soc., **37**, 108.
[2] *Ibid.*, **36**, 103.
[3] Ann. chim. phys. [3], **30**, 455.
[4] Ann. Chem. (Liebig), **230**, 221.
[5] Ber. d. chem. Ges., **25**, 3621.

formulas RNI_2, R_2NI, etc. A short time ago Remsen and Norris[1] showed that compounds of a different class were formed if water was not used as a solvent, and later one of us[2] described more in detail the action of bromine on the fatty amines in the absence of water.

It was shown that in all cases the halogen causes the complete decomposition of a part of the amine, and that the hydrobromic acid formed unites with the rest of the amine and forms a salt. In the presence of an excess of bromine a perhalide is formed of the composition $R_2NHBr.Br$ in the case of secondary and tertiary amines. The action of iodine on trimethylamine and dimethylamine was also described. Trimethylamine formed an addition-product of the formula $(CH_3)_3N.I_2$, but trimethylamine gave a perhalide, $(CH_3)_2HN.HI.I$, analogous to the perbromides.

The study of the action of iodine on the different classes of fatty amines has been continued, and facts have been discovered which have an important bearing on the composition of the compounds formed by the action of iodine on ammonia.

The composition of nitrogen iodide has occupied the attention of a number of chemists who have obtained markedly different results from its study. The last communication on the subject is by Chattaway,[3] who has reviewed the results of former workers and has studied the conditions necessary for the preparation of the compound in a pure condition. It is clearly shown that the discordant results were due to the fact that impure samples of nitrogen iodide had been investigated. As the compound cannot be crystallized and is readily decomposed by reagents, its purification is difficult. Chattaway overcame the difficulties, however, and showed that but one compound is obtained, although the method of preparation is varied. It is shown that the ratio of nitrogen to iodine is always 1 : 2, and that the compound has either the formula NHI_2, which had been previously assigned to it, or the formula NH_3I_2, which Chattaway considers the more probable from the study of its reactions. In the light of the work about to be described, the formula NH_3I_2 seems improbable.

[1] This JOURNAL, **18**, 90. [2] *Ibid.*, **20**, 51.
[3] J. Chem. Soc. (London), **69**, 1572.

Before discussing the arguments of Chattaway in favor of the above formula, a summary of the results of the study of the action of iodine on the fatty amines is necessary.

It has already been stated that iodine forms a stable addition-product with trimethylamine. This compound has some reactions like those of nitrogen iodide and has the composition $(CH_3)_3N.I_3$, similar to that proposed by Chattaway for the iodide of nitrogen. In fact Chattaway uses the existence of this compound as an argument in favor of his conception. Dimethylamine, however, does not form such an addition-product. Iodine immediately causes substitution and the hydriodic acid formed unites with the rest of the amine and forms a salt. This difference in behavior led to a study of the action of iodine on primary, secondary, and tertiary amines in order to see if the conclusions indicated by the above facts are general.

Triethylamine was first studied. Ethereal solutions of the amine and iodine were mixed and kept at a temperature below —3°. In a few minutes an oil separated, which was shown by analysis to be the periodide $(C_2H_5)_3N.HI.I_2$. The mother-liquor, on evaporation, gave triethylamine hydroiodide. The experiment was repeated, using carbon tetrachloride as the solvent in order to have present no hydrogen except that in the amine. The formation of the hydroiodide and periodide seemed to take place even more readily.

The action of iodine on an aqueous solution of the amine was next studied. The iodine was dissolved in a small amount of potassium iodide and was slowly added to the solution of the amine. A yellow solid separated which proved to be iodoform. When a large amount of iodine was added to a strong aqueous solution of the amine the periodide was precipitated.

It is seen, therefore, that iodine acts vigorously on triethylamine forming hydriodic acid as one of the products of decomposition. In the presence of water the decomposition goes so far that iodoform is formed. There were no indications of the formation of a simple addition-product. The substitution-product was evidently formed in small quantity and could not be isolated. The hydriodic acid produced by the reac-

tion reacted with the free amine present and converted nearly the entire amount of it into hydroiodide.

With tripropylamine the results were different. The oil formed by bringing together ethereal solutions of the amine and iodine was washed with ether, dried, and analyzed. The results showed that an addition-product of the formula $(C_3H_7)_3N.I_2$ was formed. From the oil prismatic crystals separated after standing some weeks. These were analyzed and found to have the composition represented by the above formula. That the compound was not a periodide similar to the dimethylamine compound, $(CH_3)_2HN.HI.I$, was shown by its stability with concentrated sulphuric acid. The crystals were entirely unaffected by the acid, whereas the periodide decomposed instantly with liberation of hydriodic acid.

As examples of secondary amines diethylamine and diamylamine were studied. When ethereal solutions of iodine and diethylamine were mixed an oil separated, and on standing some time crystals of diethylamine hydroiodide appeared. Sulphuric acid liberated hydriodic acid from the oil which was accordingly not a simple addition-product of the amine and iodine. The amine and iodine were brought together in a carbon tetrachloride solution at —10°. The hydroiodide precipitated. In aqueous solutions iodoform resulted. Analogous results were obtained when diamylamine was used. It is evident, therefore, that secondary amines do not form addition-products of the formula $R_2HN.I_2$. No attempt was made to isolate the substitution-product formed by the reaction since Raschig has shown that the compound $(C_2H_5)_2NI$ is very unstable.

Methylamine was studied as a type of primary amines. Iodine caused the immediate formation of methylamine hydroiodide in ethereal or carbon tetrachloride solution.

From the above facts the conclusion is drawn that iodine readily attacks the amines, causing substitution, and that this is accompanied by the formation of an addition-product of iodine and the amine only in the case of tertiary amines. This conclusion is inconsistent with the view of Chattaway.

A number of the arguments put forward in favor of the addition-formula for nitrogen iodide receive positive answers

from the work of previous investigators on the action of iodine on the fatty amines, the work described above, and the results of experiments in progress in this laboratory on the reactions of the iodine substitution-products of the amines.

On page 1578 Chattaway (*loc. cit.*) in speaking of the action of iodine on ammonia, says, "iodine substitutes only with extraordinary difficulty, if at all, and here we have an almost instantaneous substitution, and in a group into which iodine is not known otherwise to enter." Raschig (*loc. cit.*) has shown that iodine readily reacts with methylamine in alkaline solution, forming the substitution-product, CH_3NI_2, and the present work shows that substitution also takes place in the absence of water.

Further, "The conclusion is again strengthened by the difference in behavior of the two elements, chlorine and iodine, towards ammonia and ammonium compounds. Nitrogen chloride is only formed when chlorine acts on an ammonium salt; as long as free ammonia is present, nitrogen is liberated. On the other hand, iodine forms nitrogen iodide only in the presence of free ammonia, and it has no substituting action on an ammonium salt, even in the presence of iodic acid." This difference in action seems to be due to the well-known difference in chemical properties of the two elements. Iodine substitutes usually, however, whenever a basic substance is acted upon as is shown by its action on aniline, by which *p*-iodoaniline is readily formed. In the presence of free ammonia substitution is possible because the hydriodic acid formed immediately unites with the ammonia and is thus removed.

Further, "One would hardly expect ammonium iodide to be formed as one of the products of its detonation if it were a substitution-product." Some experiments which will be reported in full later show that the compounds CH_3NCl_2 and $(CH_3)_2NCl$ readily decompose and give the chlorides of methylamine and dimethylamine, respectively.

And finally, "If nitrogen iodide were a substitution-derivative of ammonia, one would expect to be able by suitable reagents to replace the iodine by other groups; no such replacement, however, has ever been observed. One would expect,

for example, to be able to replace the iodine by hydroxyl by the action of water or caustic alkalies, or moist oxides of silver or lead." Attempts have been made in this laboratory to prepare tetraalkylated hydrazines by the action of silver, zinc-copper couple, and sodium on the compounds $(CH_3)_2NI$, $(C_2H_5)_2NCl$, etc. In all cases negative results were obtained. The products formed always contained a large percentage of the amine from which the substitution-product had been obtained. Sodium thiosulphate readily decomposed iododimethylamine, but no hydrazine has yet been found. The action of silver oxide yielded mixtures from which no hydroxylamine derivative could be isolated. These results show that the decomposition of substitution-products is not simple. Experiments are still in progress on the above reactions and will be reported later.

As the reactions of nitrogen iodide do not speak positively for one formula or the other, it seems that the facts stated above are strong evidence which should be considered in deciding its formula. The action of iodine on the substituted ammonias can be more readily studied than its action on ammonia itself, and, as with the former addition-products are possible only when all the hydrogen of ammonia is replaced by alkyl groups, it seems highly probable that the compound with ammonia is not a direct addition-product.

The methods of preparation of nitrogen iodide and diiodomethylamine, CH_3NI_2, are analogous. This also speaks for the formula NHI_2.

As the work showed that the existence of a compound of the formula NH_3I_2 seemed improbable, the compounds made by Guthrie[1] and by Seamon,[2] and to both of which the above formula was assigned, were prepared and studied. Guthrie prepared his compound by adding powdered iodine to a saturated solution of some easily soluble ammonium salt, partially decomposed by one-third its equivalent of potassium hydroxide. Seamon passed dry ammonia over iodine cooled by melting ice, and obtained a black oil which was not explosive.

From the work on the amines it seemed probable that a substance prepared under the above conditions would be a mix-

[1] J. Chem. Soc. (London), 1863, 239. [2] Chem. News, 44, 188.

ture of a periodide and a substitution-product. Accordingly, ammonium periodide and the iodide of nitrogen were prepared and mixed. The periodide prepared by the method of Johnson[1] was a black oil. It readily dissolved large quantities of nitrogen iodide and the resulting mixture was found to have the physical properties of the compound prepared by Seamon's method.

The action of solvents on Seamon's compound and on the mixture was studied side by side. Both dissolved easily and completely in ether, although the mixture contained nearly 50 per cent of nitrogen iodide, which is insoluble in ether. Both were soluble in ethyl acetate, slightly soluble in chloroform, benzene, and carbon disulphide, and insoluble in carbon tetrachloride. When treated with water both left an explosive residue.

These facts seem to show that the action of iodine on ammonia is analogous to its action on the primary and secondary amines, and that no addition-product is formed.

In conclusion the work shows that :

1. Iodine readily attacks the fatty amines and, in the absence of water, hydroiodides and periodides are formed.

2. With some tertiary amines, addition-products of the formula $R_3N.I_2$ are formed.

3. Nitrogen iodide is not a direct addition-product of ammonia and iodine.

4. The non-explosive substance to which the formula $NH_3.I_2$ has been assigned is probably a mixture.

EXPERIMENTAL.

In all of the work to be described about molecular quantities of iodine and the amine were used, as it was thought that these conditions were the most favorable for the formation of a compound of the formula $R_3N.I_2$. A slight excess of the amine was present in order to avoid the presence of free iodine after the reaction.

Action of Iodine on Triethylamine.

Ethereal solutions of iodine and of triethylamine were mixed. In a few minutes an oil separated. This was

[1] J. Chem. Soc. (London), **33**, 397.

washed with water which did not seem to affect it and was analyzed with the following results :

0.1623 gram salt gave 0.2394 gram AgI.

	Calculated for $(C_2H_5)_3NH.HI.I_2$.	Found.
I	78.88	79.73

The substance was evidently a periodide. It was not a direct addition-product as concentrated sulphuric acid caused a vigorous evolution of hydriodic acid. When the ethereal mother-liquor from the oil was evaporated more of the oil was obtained mixed with crystals of triethylamine hydroiodide, which was identified by its melting-point, 175°–176°, and by an analysis.

The experiment was repeated care being taken to keep the temperature below —3°. The same results were obtained.

Carbon tetrachloride was next used as a solvent in order to have no hydrogen present except that in the amine. An oil was formed in which white crystals of the hydroiodide appeared on standing.

A dilute aqueous solution of triethylamine was treated with iodine dissolved in potassium iodide. The yellow precipitate formed was washed and crystallized from alcohol. An analysis of the hexagonal plates which melted at 119° showed them to be iodoform.

When strong solutions of the amine and iodine were used, a red oil precipitated, an analysis of which gave results approximating those required by the formula $(C_2H_5)_3N.HI.I_2$

In all of the experiments there was no indication of the formation of an addition-product. No substitution-product except iodoform was isolated. Iodine probably causes the complete breaking down of a part of the amine and the hydriodic acid formed unites with the rest to form a salt.

Action of Iodine on Tripropylamine.

Ethereal solutions of the amine and of iodine when mixed formed a brown solution from which an oil separated in a few minutes. This was washed with ether and dried over sulphuric acid. After standing a few days a few red fibrous crystals, which melted at 66°, appeared. The oil was dis-

solved in alcohol and ether added; a brown crystalline precipitate was thrown down, which melted at 59°–62°. The crystals were evidently a mixture which contained some tripropylamine hydroiodide, for this compound was found in the mother-liquor from which the oil had been separated. The preparation was repeated at —5°. The compound separated more slowly but did not come down in crystalline condition. The resulting oil, after standing two days, was washed with water. The results of an analysis agreed with the formula $(C_3H_7)_3NH.HI.I_2$, but there was no proof that the substance was a pure compound.

In the next experiment the oil was prepared immediately washed with ether, dried at 90°, and analyzed (Analysis I).

From the oil stout prismatic crystals separated after standing a month in a desiccator. These melted at 66° and were accordingly the same as the compound which was obtained in the first experiment. The crystals were analyzed (Analysis II).

I. 0.3208 gram salt gave 0.3687 gram AgI.

II. 0.0726 gram salt gave 0.855 gram AgI.

Calculated for $(C_3H_7)_3N.I_2$.	Found.	
	I.	II.
63.98	62.12	63.64

The compound is insoluble in ether, slightly soluble in carbon tetrachloride, soluble in ethyl acetate and chloroform. With water the crystals melt to an oil. Concentrated sulphuric acid had no action on them. The compound was therefore not a periodide.

When carbon tetrachloride was used as solvent for the amine and iodine, the oil was formed as well as a large amount of tripropylamine hydroiodide.

In aqueous solution iodine dissolved in potassium iodide precipitated an oil which gave results on analysis agreeing with the formula of the periodide $(C_3H_7)_3N.HI.I_2$.

Action of Iodine on Diethylamine.

When ethereal solutions of the amine and iodine were mixed a dark oil precipitated, and, after standing some time, crystals of diethylamine hydroiodide were formed in the solu-

tion. Concentrated sulphuric acid set free hydriodic acid from the oil which was accordingly not a simple addition-product of the amine and iodine. The same result was obtained when the solutions were kept at —5°, except that the oil separated more slowly.

When carbon tetrachloride was used as the solvent and iodine was added to the amine, a white crystalline precipitate of the hydroiodide of the amine appeared immediately. This was changed by the addition of more iodine, to a periodide, a dark-brown crystalline precipitate, which melted to an oil when brought in contact with the air. At —10° the result was the same.

In dilute aqueous solution, in the presence of sodium carbonate, iodoform was formed.

The action of iodine on the amine, without the presence of a solvent, was also investigated. At the ordinary temperature the action was violent and was accompanied by much heat and the evolution of white fumes. At —18° the two substances were inactive.

No addition-product was found as the result of the action of the two substances on each other. Under all circumstances the reaction resulted in the formation of a large amount of diethylamine hydroiodide, showing that iodine had caused substitution.

Action of Iodine on Diamylamine.

Solutions of the amine and of iodine in ether were mixed. The temperature rose and a black crystalline salt precipitated. This was washed with ether and analyzed.

I. 0.4320 gram salt gave 0.5692 gram AgI.

II. 0.3811 gram salt gave 0.5019 gram AgI.

Calculated for $(C_5H_{11})_2NH.HI.I_2$.	Found.	
	I.	II.
70.68	71.12	71.25

The periodide prepared from the hydroiodide and iodine dissolved in hydriodic acid had the appearance and properties of the salt prepared as above.

Solutions which had been cooled in a freezing-mixture were next mixed. After standing some time, diamylamine hydro-

iodide crystallized out. From the mother-liquor a dark oil separated which had the properties of periodide.

Action of Iodine on Methylamine.

Dry methylamine was passed into an ethereal solution of iodine; a black crystalline precipitate was formed which was shown by analysis to be a periodide.

As in this experiment the iodine was in excess, a solution of iodine in carbon tetrachloride was added to a solution of the amine in the same solvent. Methylamine hydroiodide separated immediately. No addition product of the amine was formed.

Action of Iodine on Ammonia.

The experiment of Seamon[1] was repeated. Dry ammonia was passed over iodine in a flask surrounded by ice. The reaction-product was a black oil which contained a small amount of a solid which was explosive when washed with ether. The oil was not explosive, however, and had the properties assigned to it by Seamon. It was soluble in ether and ethyl acetate, less soluble in chloroform, benzene, and carbon disulphide, and insoluble in carbon tetrachloride. Water decomposed it and nitrogen iodide was formed.

The substance prepared by Guthrie's[2] method was a greenish-black, thick liquid, which resembled the above compound closely.

As it seemed probable that compounds prepared as above would contain ammonium periodide and nitrogen iodide these substances were made and mixed. Ammonium periodide made according to Johnson was a black, heavy liquid. It readily dissolved nitrogen iodide, and the resulting mixture had all the properties of the substances described above. The mixture dissolved readily in ether, although nitrogen iodide is insoluble in this solvent.

BOSTON, MASS., February, 1899.

[1] *Loc. cit.* [2] *Loc. cit.*

Contributions from the Chemical Laboratory of Harvard College.

CXII.—ON THE ACTION OF SODIC ETHYLATE ON TRIBROMDINITROBENZOL.[1]

By C. Loring Jackson and Waldemar Koch.

The principal object of the work described in this paper was to determine the constitution of the dinitroresorcine diethylether melting at 133°, formed by the action of a hot solution of sodic ethylate on tribromdinitrobenzol, ($Br_3$1,3,5,(NO_2)$_2$2,4), or on the bromdinitroresorcine diethylether melting at 184°. This determination was of interest to us, as it formed part of an investigation of the replacement of bromine by hydrogen under the influence of sodium malonic ester, sodic ethylate, and similar reagents, which has now been in progress for several years in this laboratory. In all the cases studied here, with a single exception, the atom of bromine (or iodine) has stood between two radicals, each in the ortho position to it and it was necessary to determine whether this arrangement also existed in this case, since a consideration of the possibilities shows that this dinitroresorcine diethylether might have either the symmetrical structure, if the bromine between the two nitro groups was replaced by hydrogen, or the adjacent structure, if this replacement occurred with one of the other atoms of bromine.

The constitution of the diethylether was determined by saponifying it to the corresponding dinitroresorcine, which proved to be the symmetrical compound, (OH)$_2$1,5(NO_2)$_2$2,4, melting at 212°.5, according to Typke.[2] The proof that this body has the structure assigned to it has been given by Nietzki and Schmidt,[3] who converted it into diimidoresorcine, which in turn yielded dioxyquinone by treatment with sodic hydrate, and this dioxyquinone gave with nitric acid nitranilic acid, which is paradinitrodioxyquinone, a result that is in harmony only with the symmetrical structure for the dinitroresorcine. It follows therefore that the bromine replaced by hydrogen in tribromdinitrobenzol is the one between the two nitro groups, as we had expected from the results of pre-

[1] Presented to the American Academy of Arts and Sciences, Oct. 12, 1898.

[2] Ber. d. chem. Ges., 16, 552. [3] *Ibid.*, 21, 2374.

vious experiments, and that the bromdinitroresorcine diethylether melting at 184° has the constitution $(OC_2H_5)_2$1,5,Br3.$(NO_2)_2$2,4. It is an interesting fact in this connection that an isomeric bromdinitroresorcine diethylether (having the constitution $(OC_2H_5)_2$1,3,Br5,$(NO_2)_2$2,4), in which the bromine is not in the ortho position to two nitro groups, gave no replacement of the atom of bromine by hydrogen, but, when treated with sodic ethylate, gave dinitrophloroglucine triethylether by the replacement of the bromine by an ethoxy group. Beilstein, in the third edition of his Handbuch, provisionally places the diethylether, $C_6H_2(OC_2H_5)_2(NO_2)_2$, melting at 133°, and the corresponding dimethylether, $C_6H_2(OCH_3)_2(NO_2)_2$, melting at 167°, prepared from tribromdinitrobenzol by W. H. Warren and one of us,[1] under the adjacent dinitroresorcine. The determination of the constitution of the diethylether just given necessitates their transfer to the symmetrical dinitroresorcine, as there can be no question that the methylether has the same structure as the ethyl compound. It also shows that the dimethylether, $C_6H_2(OCH_3)_2(NO_2)_2$, melting at 67°, prepared by Hönig[2] by the direct action of nitric acid on a solution of resorcine dimethylether in glacial acetic acid, cannot have the symmetrical structure which Beilstein assigned to it, as this now belongs to the body melting at 167°.

In addition to this determination of the constitution of dinitroresorcine diethylether, we have made a more careful study of the products of the reaction between sodic ethylate and tribromdinitrobenzol melting at 192° both at ordinary temperatures and when aided by heat. These reactions had already been studied by W. H. Warren and one of us,[3] with the result that in the cold the bromdinitroresorcine diethylether melting at 184° was formed, whereas, when hot, the dinitroresorcine diethylether melting at 133° was the product isolated. As, however, subsequent work[4] upon the tribromtrinitrobenzol showed that in that case the action was far from simple, it hardly seemed probable that the dinitro compound had given only one organic product in each of these cases, and this inference wrs confirmed by our first new ex-

[1] This JOURNAL, **13**, 170, 179.
[2] Ber. d. chem. Ges., **11**, 1041.
[3] This JOURNAL, **13**, 167.
[4] Jackson and Warren: *Ibid.*, **15**, 607.

periment in this field, as we found sodic nitrite as well as sodic bromide among the products of the reaction, so that it was evident that some other compounds were present beside those recognized by Warren and one of us. The result of this later work was the isolation of the following products of the action of sodic ethylate on tribromdinitrobenzol, melting-point 192°, when absolute alcohol and benzol are used as the solvents, and the mixture is allowed to stand at ordinary temperatures:

(1) Bromdinitroresorcine diethylether, $C_6HBr(OC_2H_5)_2(NO_2)_2$, melting at 184°, $(OC_2H_5)_2$1,5,Br3$(NO_2)_2$2,4.

(2) Bromdinitroresorcine diethylether, $C_6HBr(OC_2H_5)_2(NO_2)_2$, melting at 92°, $(OC_2H_5)_2$1,3,Br5,$(NO_2)_2$2,4.

(3) Tribromnitrophenol, $C_6HBr_3(NO_2)OH$, melting at 90°, $Br_3$1,3,5,$NO_2$2,OH4.

(4) Dinitroresorcine monoethylether, $C_6H_2(OC_2H_5)OH(NO_2)_2$, melting at 77°, (OC_2H_5)1,OH_5,$(NO_2)_2$2,4.

(5) Dinitrophloroglucine triethylether, $C_6H(OC_2H_5)_2(NO_2)_2$, melting at 105°, $(OC_2H_5)_2$1,3,5,$(NO_2)_2$2,4.

These products indicate that there are three primary reactions, when sodic ethylate acts on tribromdinitrobenzol. These are, Reactions I. and II., consisting in the replacement of two atoms of bromine by two ethoxy groups, producing the two isomeric bromdinitroresorcine diethylethers (1) and (2), and Reaction III., in which one nitro group is replaced by one hydroxyl group (or by an ethoxy group followed by saponification) giving the tribromnitrophenyl (3). There are also two secondary reactions owing to the further action of sodic ethylate on the products of Reactions I. and II.; first, the replacement of the bromine in the bromdinitroresorcine diethylether (1) by an atom of hydrogen (followed by partial saponification) giving the dinitroresorcine monoethylether (4); and secondly, the replacement of the bromine in the bromdinitroresorcine diethylether (2) by the ethoxy group, giving the dinitrophloroglucine triethylether (5). The saponification mentioned in this paragraph might be brought about by the sodic hydrate formed from the sodic ethylate by the water added in the course of the purification, but it seems to us more probable that the phenols were formed by some

sodic hydrate acting directly on the tribromdinitrobenzol, since the ethers of the phenols seemed decidedly stable, when treated with an alkali.

The following estimations of the approximate yields of the products give a rough idea of the extent to which each of the three primary reactions ran:

	Per cent.
Reaction I., forming substances (1) and (4)	28
Reaction II., forming substances (2) and (5)	38
Reaction III., forming substance (3)	1
Total	67

As most of these substances were purified by crystallization, too much weight must not be given to these yields, but we can safely infer from them that Reaction II. ran to the largest extent, Reaction I. came next, and Reaction III. took place only to a very limited extent.

These results are capable of a satisfactory theoretical explanation, but before giving this it will be well to consider a parallel case studied by W. H. Warren and one of us,[1] in which the conditions are simpler and rather better marked. This is the action of sodic ethylate on symmetrical tribromtrinitrobenzol, $C_6Br_3(NO_2)_3(Br_3{}^{1,3,5},(NO_2)_3{}^{2,4,6})$ which consisted of two simultaneous reactions, first, the replacement of two nitro groups by two ethoxy groups, giving $C_6Br_3NO_2(OC_2H_5)_2$, and second, the replacement of the three bromine atoms by three ethoxy groups, giving $C_6(C_2H_5)_3(NO_2)_3$. These two reactions ran to nearly an equal extent (about 45 per cent of each product), if the solvent was alcohol only.[2] In attempting to explain these experimental results we must consider the agencies which tend to loosen the nitro groups on the one hand and the atoms of bromine on the other from the benzol ring. We have designated these agencies by letters, and arranged them in the order of intensity, beginning with the strongest.

A. The loosening effect of the three nitro groups on the three atoms of bromine. This is a strong agency, as shown

[1] This JOURNAL, 15, 619.

[2] If the solvent was benzol and alcohol, less of the nitro groups were replaced; but this case need not be considered in this discussion.

by the fact that picryl chloride (in which the chlorine is similarly disposed to the three nitro groups) is decomposed easily and completely, even at ordinary temperatures.[1]

B. The loosening effect exerted by the three nitro groups on each other. Lobry de Bruyn[2] has shown that symmetrical trinitrobenzol is converted into dinitroanisol by sodic methylate, even at ordinary temperatures; this loosening effect is therefore a powerful one, but not quite so strong as *A*, since the action of picryl chloride is complete in a few minutes, whereas the reaction with trinitrobenzol needs several days, if carried on in the cold.

C. The loosening effect of the three atoms of bromine on the three nitro groups. This is a much weaker action than *B*, since with the tetrabrombenzol,[3] ($Br_4$1,2,4,6), the atom of bromine (which stands in the same position toward the three atoms of bromine as the three nitro groups do in our compound) was removed only after long boiling of the benzol and alcohol solution with sodic alcoholate, and then incompletely.

D. The loosening effect of the three bromine atoms on each other. This is a feeble effect, as Blau[4] found it necessary to heat symmetrical tribrombenzol to 120°–130° with sodic methylate to obtain much action. Calvert and one of us[5] found that with sodic ethylate a reaction took place at the boiling-point of alcohol in open vessels, but the reaction ran more slowly, and was less complete than that with tetrabrombenzol.

We have then the most powerful loosening effect *A*, and the weakest loosening effect *D*, exerted on the atoms of bromine, while the two intermediate effects *B* and *C* influence the nitro groups, so that $A + D$ is very nearly, if not quite, equal to $B + C$; that is, the attack of the sodic ethylate will be directed about equally upon the atoms of bromine and upon the nitro groups, which was the result of our experimental work as stated above.

A similar discussion of the action of sodic ethylate on tribromdinitrobenzol gives the following results. The loosening effects are marked by letter, and arranged in order of intensity as before.

[1] This JOURNAL, **20**, 447. [2] Rec. Trav. Chim. Pays-Bas., **9**, 208.
[3] Jackson and Calvert: This JOURNAL, **18**, 309.
[4] Monatsh. f. Chem., **7**, 630. [5] This JOURNAL, **18**, 310.

E. The action of the two nitro groups in loosening the three atoms of bromine. This is a strong effect, as shown by the ease with which the bromdinitrobenzol, $Br1(NO_2)_2 2,4$, is decomposed by potassic hydrate.[1]

F. The effect of the three atoms of bromine on the two nitro-groups already discussed.

G. The effect of the three atoms of bromine on one another, which has also been considered in the previous discussion.

H. The effect of the two nitro groups on each other. So far as we can find, this effect is too feeble to produce a replacement of the nitro group by an ethoxy group, but it should not be left out of account, as Lobry de Bruyn[2] has found that potassic cyanide in alcoholic solution converts metadinitrobenzol into $C_6H_3NO_2OC_2H_3CN$, which shows a certain loosening of one of the nitro groups.

Here then we have only one strong loosening agency (*E*), and this acts on the atoms of bromine, while of the other three by far the feeblest (*H*) is one of those acting on the nitro groups. It is evident therefore that

$$E + G > F + H,$$

or, putting it into words, the attack upon the nitro groups will be insignificant compared to that on the atoms of bromine. This is in accord with our experimental results already given, since the attack on the nitro groups (Reaction III.) was to the attack on the atoms of bromine (Reactions I. and II.) as 1 to 66.

From the yields of the two bromdinitroresorcine diethylethers, given earlier in this paper, it is possible to draw conclusions in regard to the effect of the position of the nitro groups in loosening the atoms of bromine, but there is some question whether such conclusions are valid, since the difference between the yields of the two bromdinitroresorcine diethylethers is only ten per cent, and this amount is within the probable limit of error in this case, where the purifications were made by crystallization. On the other hand, the product melting at 92° (2) was obtained in the larger quantity, and this is the one where we should expect the greatest loss,

[1] Clemm : Jour. Pr. Chem., [2], 1, 145. [2] Rec. Trav. Chim. Pays-Bas, 2, 205.

since in its purification the crystallizations were the most numerous. We feel, therefore, justified in giving the following discussion with all necessary reserve. In the two reactions (I. and II.) one of the atoms of bromine replaced occupied in each case the same position (ortho-para) toward the nitro groups, and therefore the difference between the reactions depends on the position of the second atom of bromine replaced. In Reaction I. this atom of bromine was ortho to one nitro group and para to the other, and this reaction gave 28 per cent of the product compared to 38 per cent from Reaction II., in which the atom of bromine was in the ortho position to both nitro groups. It would seem therefore, that the diortho position of the nitro groups exerted a stronger loosening effect upon the bromine than the orthopara position.

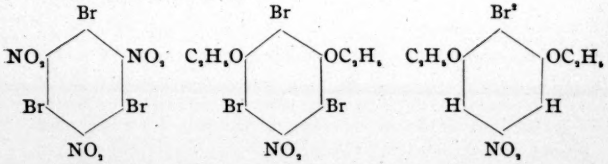
When the reaction between tribromdinitrobenzol and sodic ethylate is carried on at 70°, the products isolated by us were the dinitroresorcine diethylether melting at 133°, a little of the bromdinitroresorcine diethylether melting at 184°, and much of the isomeric substance melting at 92°. These were the only products we have succeeded in identifying, although we obtained indications of the presence of the tribromnitrophenol. There was also a crystalline substance melting at 212°, but in too small quantity for identification, and a great deal of tarry matter. The absence of the dinitrophloroglucine triethylether is surprising; we should account for it by supposing that the reaction ran for so short a time (ten minutes) that the bromdinitroresorcine melting at 92° did not undergo decomposition. The hypothesis that the phloroglucine ether formed was converted into tarry substances by the hot sodic ethylate seems to us less probable. The approximate yields of the two products of the reaction at 70° were:

	Per cent.
Dinitroresorcine diethylether, melting-point 133°	16
Bromdinitroresorcine diethylether, melting-point 92°	9
Total	25

So that in this case 75 per cent of the substance was unaccounted for. Most of this undoubtedly went into the tarry products.

The most striking phenomenon in the action of sodic ethylate on tribromdinitrobenzol at high temperatures is the replacement of hydrogen of the atom of bromine in the ortho position to both nitro groups. The fact that this reaction only takes place to a very limited extent in the cold may perhaps be accounted for by the sparing solubility of the bromdinitroresorcine diethylether melting at 184° in the cold alcohol and benzol, so that most of it is precipitated, and therefore removed from the action of the ethylate. On the other hand, as this ether is easily soluble in these liquids, when hot, it would be brought into the sphere of the reaction under these conditions, and the dinitroresorcine diethylether would be formed. The bromdinitroresorcine diethylether melting at 92° is soluble in the cold solvents, and this probably accounts for the fact that a considerable amount of it was converted into the dinitrophloroglucine triethylether even in the cold.

It is perhaps worth while to call attention to the fact that in the reactions described in this paper the action is confined either to the atoms of bromine or to the nitro groups; that is, if it has started in one set of radicals in the meta position to each other, it does not extend to the other set of radicals in the meta position to each other and ortho or para to the first set. This observation has been made frequently in the course of the investigation of which this is a part, and the principle has sometimes given valuable aid in interpreting experimental results. In only a single case has such an extension of the reaction beyond the limits of the first set of trimeta positions been observed; this was in the action of hot sodic ethylate on tribromtrinitrobenzol,[1] which gave first tribromnitroresorcine diethylether, and by further action bromnitroresorcine diethylether



[1] This JOURNAL, 15, 640.

[2] The position of the atom of bromine in this substance has not been established experimentally.

We are not, however, inclined to be too sure of the general occurrence of this restriction of reactions to a single trimeta zone, since the exceptional action just mentioned, in which the second trimeta zone was invaded, was accompanied by the formation of much tarry matter, and therefore it is possisible that the tarry products so frequent in these reactions may have been formed by similar invasions of the second trimeta zone. The bearing of these observations on the benzol formula of J. N. Collie[1] is obvious.

Preparation of Symmetrical Tribromdinitrobenzol.

The description of the preparation of tribromdinitrobenzol is scattered through a number of papers from this laboratory, so that it would be a matter of some difficulty to find it, and there would be danger that anyone looking it up might not find the latest and best form of the process; we have thought it well, therefore, to give here a connected account of this process.

To make tribromaniline, 60 grams of aniline were treated with dilute hydrochloric acid, and dissolved in four liters of water. Then a rapid stream of air saturated with bromine vapor was drawn through the liquid by means of a Bunsen pump, until it assumed a distinct yellow color, which did not change for several minutes. The amount of bromine required was about 320 grams. The precipitate of tribromaniline was filtered out through cheese-cloth, washed until free from acid and dried by pressing with a screw press, followed by heating to about 60° over a steam radiator.

To convert this tribromaniline into tribrombenzol, 100 grams of it were dissolved in 600 cc. of alcohol and 150 cc. of benzol by the aid of heat; 40 cc. of common strong sulphuric acid were then added to the hot solution from a pipette, and any precipitate formed was dissolved by longer heating, or even adding more of the solvents. Forty grams of finely powdered sodic nitrite were next sifted into the hot solution as rapidly as the violence of the reaction permitted, and the product heated, until there was no more effervescence, after which it was allowed to stand at ordinary temperatures over night, and then filtered and dried.

[1] Proc. Chem. Soc., 1896-1897, p. 143.

The tribrombenzol was converted into tribromdinitrobenzol as follows: The perfectly dry tribrombenzol was mixed with four or five times its weight of fuming nitric acid of specific gravity 1.51, and gently heated over a low flame for two hours in a flask closed with a porcelain crucible, taking care that the temperature was kept just below boiling. It was then allowed to stand over night at ordinary temperatures, when most of the tribromdinitrobenzol crystallized out, while the rest of it was obtained by pouring the supernatant acid liquid into a large excess of water. The dried product was purified by crystallization from about eight times its weight of a mixture of three parts of alcohol with one of benzol.

Action of Sodic Ethylate on Tribromdinitrobenzol at 70°.

The tribromdinitrobenzol used in all this work, made in the way described in the previous section, melted at 192°, and had the constitution $Br_3,1,3,5,(NO_2)_2,2,4$. Forty grams of this tribromdinitrobenzol were dissolved in 80 cc. of benzol, and mixed with the solution of sodic ethylate obtained from 6.8 grams of sodium and 180 cc. of absolute alcohol, which gave the proportion of three molecules of sodic ethylate to each molecule of tribromdinitrobenzol. The flask containing the mixture was then placed in a water-bath, which was heated until a thermometer immersed in the mixture rose to 70°, at which temperature the solution was kept for ten minutes. The liquid turned dark brown during this heating, a color which had been found to be characteristic of the reaction with the aid of heat. At the end of the ten minutes the liquid was poured into a large evaporating dish, and the solvents allowed to evaporate spontaneously. The residue thus obtained was washed with water until the wash-water became colorless, and the product purified as follows.

Residue Insoluble in Water.

This residue was dried and extracted three times with boiling ligroin. The portion insoluble in ligroin was purified by repeated crystallization from a mixture of ligroin and benzol, during which it was frequently treated with bone-black. The product was the dinitroresorcine diethylether already ob-

tained in this way by W. H. Warren and one of us;[1] it was recognized by its melting-point, 133°, and its solubilities and appearance.

The ligroin solution on standing deposited a flocculent precipitate in too small quantity for identification, which was filtered out, and the filtrate evaporated to dryness; the crystalline residue was spread on an unglazed plate to remove oily impurities, after which it was purified by crystallization from hot ligroin. After four crystallizations it showed the constant melting-point 92°, when it was dried *in vacuo*, and analyzed with the following result:

I. 0.2043 gram of the substance gave by the method of Carius 0.1136 gram of argentic bromide.

II. 0.2885 gram of the substance gave 20.6 cc. of nitrogen at a temperature of 12° and a pressure of 745 mm.

	Calculated for $C_6HBr(OC_2H_5)_2(NO_2)_2$.	Found. I.	II.
Bromine	23.89	23.69	....
Nitrogen	8.36	....	8.32

The substance is therefore a bromdinitroresorcine diethylether isomeric with the one obtained by W. H. Warren and one of us[2] by the action of cold sodic ethylate upon the tribromdinitrobenzol and melting at 184°. As the constitution of this substance has been established (in this paper) as $OC_2H_1{}^1OC_2H_5{}^3Br_3{}^5NO_2{}^2NO_2{}^4$, it follows that our new bromdinitroresorcine diethylether must have the constitution

$$OC_2H_1{}^1OC_2H_3{}^3Br_5{}^5NO_2{}^2NO_2{}^4,$$

as this is the only other body with this composition which can be obtained from the tribromdinitrobenzol.

Properties of Bromdinitroresorcine Diethylether. Melting-point 92°.

$C_6HBr(OC_2H_5)_2(NO_2)_2$. $(OC_2H_5)_2{}^{1,3}Br_5{}^5(NO_2)_2{}^{2,4}$.

This substance crystallizes in white needles thickly crowded into bunche sshaped like hour-glasses; when better developed, they form prisms with blunt ends, which seem to be made up of a basal plane modified by very minute planes of a pyramid. On long exposure to the air, especially in bright light, it

[1] This JOURNAL, 13, 170. [2] *Ibid.*, 13, 167.

turns brownish, and this change is accompanied by decomposition. It melts at 92°; and is freely soluble even in the cold in benzol, ether, chloroform, acetone, glacial acetic acid, carbonic disulphide, or acetic ester; somewhat soluble in cold alcohol, freely in hot; sparingly soluble in cold ligroin, freely in hot; essentially insoluble in water whether cold or hot. Ligroin is the best solvent for it. A hot solution of sodic hydrate has little or no action on it. On heating it with sodic ethylate it is converted almost quantitatively into the triethylether of dinitrophloroglucine formed by the replacement of its atom of bromine by an ethoxy group; the product was recognized by its melting-point, 105°, and its other properties. The wash waters gave no test for a nitrite, showing that the nitro groups had not been attacked.

Other Products of the Reaction.—During the purification of the dinitroresorcine diethylether a small quantity of the bromdinitroresorcine diethylether melting at 184° was isolated. Its presence shows that the heating for ten minutes used by us was not sufficient to convert the whole of it into the dinitroresorcine diethylether.

From the ligroin mother-liquors of the bromdinitroresorcine diethylether melting at 92°, a few milligrams of a body were obtained, which melted constant at 112°, contained bromine, and gave no test for nitrogen after fusion with sodium.[1] We supposed, therefore, that we had the tribromresorcine, which melts according to Benedikt at 111°, and could be formed by the replacement of the two nitro groups by ethoxy radicals, followed by saponification; but upon comparing our specimen with some tribromresorcine made for this purpose, it was found that, although the two substances melted at the same point, (as we found the melting-point 112°–113° for the tribromresorcine), they differed markedly in solubility in alcohol, our substance being much less soluble, and also in the method of crystallization, although the forms were not incompatible. That our substance was not tribromresorcine was proved by the action of sodic hydrate, which did not affect our body, whereas it dissolved the tribromresorcine instantly, giving a solution which turned black almost at once.

[1] We do not feel that this proves the substance is free from nitrogen.

The amount of our substance was not enough for analysis, so we can make no statement in regard to its nature. We add a description of its crystalline form, which may lead to its identification. It forms when crystallized from alcohol white very sharp needles, which when better developed appear as slender prisms with square ends or bluntly sharpened by several planes at very obtuse angles to the sides and terminated by a basal plane. When less well developed, it forms felted masses of needles or bunches, or long sheaves of needles. None of the arborescent forms were observed which seemed to be characteristic of the tribromresorcine. This substance was also characterized by its solubility in ligroin. It was only formed in very minute quantities under the conditions of the reaction used by us.

The Products of the Reaction Soluble in Water.

The wash-waters obtained from the product of the action of sodic ethylate on tribromdinitrobenzol at 70° were highly colored, but the substances obtained by acidifying them with acetic acid were so tarry that we could not isolate any body fit for analysis. The filtrate from this tar, which was also colored, was evaporated to small bulk, and treated with baric chloride, when a gelatinous precipitate was obtained, which resembled the barium salt of tribromnitrophenol described later in this paper. We did not, however, succeed in getting enough of it to purify for analysis.

The approximate yields of the principal products of the action of sodic ethylate on tribromdinitrobenzol at 70° were determined as follows:

	Per cent.
Dinitroresorcine diethylether	16
Bromdinitroresorcine diethylether melting at 92°	9
Total	25

From which it appears that 75 per cent of the theoretical yield had been converted into the tarry mass, from which we could isolate nothing fit for analysis.

Action of Sodic Ethylate upon Tribromdinitrobenzol in the Cold.

The proportions used were the same as those used in the

experiment at 70°, that is, 40 grams of the tribromdinitrobenzol dissolved in 80 cc. of benzol and mixed with the sodic ethylate from 6.8 grams of sodium and 180 cc. of absolute alcohol. The mixture was allowed to stand in a corked flask from three to five days with frequent shaking, after which it was poured into an evaporating dish, and allowed to evaporate spontaneously. The residue was washed with water until the washings were colorless, and the products were then purified as follows.

Residue Insoluble in Water.

This was dried and extracted three times with boiling ligroin, which left a crystalline residue, and this after recrystallization from a mixture of alcohol and benzol showed the constant melting-point 184°, and was therefore the bromdinitroresorcine diethylether discovered by W. H. Warren and one of us in the previous work on this reaction.

The ligroin extract was allowed to stand over night, when it deposited crystals, which were filtered out, and strangely enough proved to be essentially insoluble in ligroin. As they could not have been formed in the ligroin solution, we can explain the extraction of them by hot ligroin only by supposing they are soluble in a mixture of ligroin and the other (soluble) product of the reaction. The crystals after purification by crystallization from a mixture of alcohol aud benzol showed the constant melting-point 105°, which suggested that they were the dinitrophloroglucine triethylether discovered by W. R. Lamar and one of us.[1] To settle the nature of the substance, it was dried at 100° and analyzed with the following result:

0.2297 gram of the substance gave 19.4 cc. of nitrogen at a temperature of 23° and a pressure of 750 mm.

	Calculated for $C_6H(OC_2H_5)_3(NO_2)_2$.	Found.
Nitrogen	9.34	9.42

It is therefore the dinitrophloroglucine triethylether.

The ligroin mother-liquor, from which the dinitrophloroglucine triethylether had been deposited, was evaporated to dryness, and spread on a porous plate to remove oily impuri-

[1] This JOURNAL, **18**, 670.

ties, after which it was dissolved in hot ligroin and allowed to crystallize, when in addition to the square prisms of dinitrophloroglucine triethylether long needles with square ends were observed, which resembled the bromdinitroresorcine diethylether melting at 92°, obtained by the action of a hot sodic ethylate solution on tribromdinitrobenzol, as described earlier in this paper. The isolation of this substance from the mixture of crystals proved a matter of great difficulty. Hot ligroin did not accomplish this, and a number of other solvents were tried with no better results. Finally, on soaking the mixture for some time with cold ligroin, it was found that a considerable amount of the square prisms remained undissolved; these were filtered out, and the filtrate on evaporation gave a residue, which was once more extracted with cold ligroin in the same way. The second extract yielded crystals, which could be purified by crystallization from hot ligroin, when their constant melting-point, 92°, and their solubilities and crystalline form proved that they were the bromdinitroresorcine diethylether $(OC_2H_5)_2{}^{1,3}Br_5{}^{1}(NO_2)_2{}^{2,4}$.

Although the dinitrophloroglucine triethylether was formed freely in the cold, we obtained none of it when we carried on the reaction at 70°. This was probably due to the short duration of our experiments (ten minutes), as there is little doubt that this substance is produced by the further action of the sodic ethylate on the bromdinitroresorcine diethylether at first formed. It follows that the best way of making the diethylether melting at 92° is the process described under the action of sodic ethylate at 70°.

Products of the Reaction Soluble in Water.

The first step in purifying the products of the reaction of sodic ethylate on tribromdinitrobenzol in the cold consisted in washing with water; the highly colored wash-waters were concentrated and acidified with acetic acid, which produced a flocculent precipitate; this was dissolved in dilute alcohol, filtered, and the hot filtrate treated with an aqueous solution of baric hydrate. On cooling, beautiful, leaf-like, lemon-yellow crystals of a barium salt separated, which, after purifica-

tion by recrystallizing from water, were dried at 100°, and the barium determined with the following result :

0.3916 gram salt gave 0.1446 gram of baric sulphate.

	Calculated for $[C_6H_2(OC_2H_5)(NO_2)_2O]_2Ba_2H_2O$.	Found.
Barium	21.78	21.71

The retention of the two molecules of water at 100° is certainly strange, especially as the salt changed from lemon-yellow to orange on heating, evidently from loss of water, and, as therefore this analysis was not sufficient to establish the identity of the substance, we prepared the free phenol by decomposing the barium salt with acetic acid. It was recrystallized from alcohol, until it showed the constant melting-point 77°, when it was dried *in vacuo*, and analyzed with the following result :

0.2125 gram of the substance gave 22.1 cc. of nitrogen at a temperature of 15° and a pressure of 752 mm.

	Calculated for $C_6H_2OHOC_2H_5(NO_2)_2$.	Found.
Nitrogen	12.28	12.11

The body is therefore a dinitroresorcine monoethylether, and seems to be identical with that discovered by Aronheim[1] by treating nitrosoresorcine ethylether with nitric acid, as the descriptions of the appearance and solubilities of the two bodies coincide, but Aronheim gives the melting-point 75°, whereas we found 77°. It seemed necessary therefore to establish the identity of our body more firmly, and this was done by saponifying a specimen of it by boiling for half an hour with a sulphuric acid of specific gravity 1.44. As the dinitroresorcine thus obtained melted at 212°, our body has the symmetrical structure

$$OH1.OC_2H_5.NO_2.NO_24,$$

and is the monoethylether corresponding to the diethylether formed by the action of hot sodic ethylate on tribromdinitrobenzol (see later in this paper). Whether our substance is identical with that discovered by Aronheim, or the difference of two degrees in the melting-point is caused by a difference in constitution, we are unable to determine with our present knowledge.

[1] Ber. d. chem. Ges., 12, 32.

The filtrate, from which the dinitroresorcine monoethyl-ether had been precipitated by acetic acid, still contained a phenol to judge by its color, and to obtain this hydrochloric acid was added, which produced a white precipitate. Without filtering, the liquid was extracted with ether, and, as this removed almost all of the color, the aqueous liquid was thrown away. The ether on evaporation usually left a red oily mass, which obstinately refused to crystallize; on one occasion, however, we succeeded in obtaining about half a gram of a solid, which after recrystallization from alcohol showed the constant melting-point 90°, and agreed in its properties with those described for the tribromnitrophenol, which melts at 89° according to Daccomo.[1] To characterize the substance more thoroughly some of the oily mass was treated with a solution of baric hydrate, and the barium salt formed, which had a gelatinous consistency, was washed with cold water, dissolved in cold alcohol, from which it was allowed to crystallize, and after being dried at 100° analyzed with the following result:

0.1816 gram of the salt gave 0.0485 gram of baric sulphate.

	Calculated for $(C_6HBr_3NO_3O)_2Ba$.	Found.
Barium	15.45	15.70

There can be no doubt, therefore, that the phenol is tribromnitrophenol formed from tribromdinitrobenzol by the replacement of one of the nitro groups by one hydroxyl radical. Our substance also shows two characteristic properties, which have been observed in the case of the tribromnitrophenol; these are the solubility of its barium salt in alcohol, and the fact that the sodium salt is not decomposed by organic acids. The constitution of the phenol follows from its mode of formation from tribromdinitrobenzol melting at 192°. It is $Br_3$1,3,5,OH2.$NO_2$4.

The following statement of the yields of these various products of the action of cold sodic ethylate on tribromdinitrobenzol will give a general idea of the extent to which each of the reactions takes place, but it should be remembered that these numbers are approximate estimates rather than strict

[1] Ber. d. chem. Ges., 18, 1167.

determinations, as must necessarily be the case where the products are purified by crystallization. The numbers are percentages of the theoretical yield in each case:

	Per cent.
$C_6HBr(OC_2H_5)_2(NO_2)_2$, melting-point 184°	22
$C_6HBr(OC_2H_5)_2(NO_2)_2$, melting-point 92°	19
$C_6H(OC_2H_5)_3(NO_2)_2$, melting-point 105°	19
$C_6H_2(OC_2H_5)OH(NO_2)_2$, melting-point 77°	6
$C_6HBr_2(NO_2)OH$, melting-point 90°	1
Total	67

It appears from this that the principal reaction is that which forms the bromdinitroresorcine diethylether melting at 92°, since the dinitrophloroglucine triethylether must be formed from this by a secondary reaction, and the yield of the two together is 38 per cent. Next after this comes the reaction forming the bromdinitroresorcine diethylether melting at 184°, and its decomposition-product, the dinitroresorcine monoethylether, as these together make up 28 per cent of the theoretical yield, while the third primary reaction, that which forms the tribromnitrophenol, is of very inferior importance, yielding only 1 per cent. These results also make it probable that no other product was formed in any considerable amount, as the percentage unaccounted for (33) is no greater than the loss which would be expected from such numbers of crystallizations, and other wasteful methods of purification as were necessary in isolating the substances enumerated. Small quantities of oily products were observed at various points in the work, as stated in the description of the purification, but except for these all the products were recognized.

Constitution of the Dinitroresorcine Diethylether Melting at 133°.

The dinitroresorcine diethylether was boiled for some time with sulphuric acid of specific gravity 1.44 in a flask with a return cooler. The reaction runs smoothly, and gives an almost quantitative yield of the symmetrical dinitroresorcine $(OC_2H_5)_2$1,5,$(NO_2)_2$2,4. This was recognized by its melting-point 210°–211°; Typke[1] gives 212°.5, Schiaparelli and Abelli[2]

[1] Ber. d. chem. Ges., 16, 552. [2] *Ibid.*, 16, 872.

214°.5, both of which are higher than that observed by us; but, as only two dinitroresorcines could be formed from tribromdinitrobenzol, the symmetrical one, whose melting-point is given above, and the adjacent, which melts at 142°, there can be no doubt about the identity of our substance. Many of its other properties also coincide with those given for symmetrical dinitroresorcine. It formed vitreous yellowish prisms apparently belonging to the monoclinic system when crystallized from acetic ester, but crystallized from alcohol in the spear-head forms, which were obtained by Typke from sublimation. The sodium salt was orange-red, the ammonium salt yellow prisms, the silver salt a red precipitate which soon turned brown. The acid barium salt consisted of rather thick yellow needles. We did not succeed in getting the carmine-red neutral barium salt. The free phenol decomposes carbonates.

THE ACTION OF SULPHOCARBANILIDE ON CERTAIN ACID ANHYDRIDES.

By Frederick L. Dunlap.

In a previous article[1] the results were given of a study of the action of sulphocarbanilide on the anhydrides of phthalic and succinic acids. It was found that when phthalic anhydride and sulphocarbanilide were heated, in molecular proportions, to a temperature of 125°–130°, the resulting products were phthalanilic acid and phenyl mustard oil; if the temperature, however, was raised to 170°–175°, the products were phthalanil, carbonic oxysulphide, and aniline. When equal molecular proportions of succinic anhydride and sulphocarbanilide were heated together succinanil, carbonic oxysulphide and aniline were obtained; but the formation of succinanilic acid and phenyl mustard oil (corresponding to the formation of phthalanilic acid and phenyl mustard oil) was not observed.

A further study of the action of sulphocarbanilide on succinic anhydride has, however, shown that by a correct regulation of the temperature, the formation of succinanilic acid and

[1] This Journal, 18, 332.

phenyl mustard oil as final products, may be brought about.

Succinanilic Acid.—Equal molecules of succinic anhydride and sulphocarbanilide were mixed intimately by grinding together to a fine powder. This mixture was heated in a small Erlenmeyer flask placed in a Victor Meyer constant-temperature bath. The liquid in this bath was water, and during the experiment the temperature kept constant at 95°–96°. After heating the mixture of sulphocarbanilide and succinic anhydride for one and a half hours, it had begun to soften and the odor of phenyl mustard oil was plainly discernible. After three hours' heating the mixture had completely melted down. The entire length of heating was six hours. After cooling, the contents of the flask were treated with a few cubic centimeters of cold alcohol to dissolve out the phenyl mustard oil present. The residue was then treated with ammonia, and all dissolved excepting a very small amount. After filtering, hydrochloric acid threw down a white crystalline precipitate. This product crystallized from water in bunches of short prisms and, when pure, had a melting-point of 144.5°–145.5°. Menschutkin[1] gives the melting-point as 138.5° and Gerhardt and Laurent[2] as 155°.

This substance was dried at 100° and, upon analysis, gave the following results:

0.2307 gram of substance gave 15 cc. of nitrogen at 13.6° C. and 737.8 mm. pressure.

	Calculated for $C_{10}H_{11}O_3N$.	Found.
N	7.25	7.47

Succinanilic acid is readily soluble in acetone and alcohol, very slightly soluble in ether, and insoluble in ligroin, chloroform, benzene, and carbon bisulphide.

The preparation of succinanilic acid in this way was the outcome of a number of experiments to obtain the addition-product of succinic anhydride and sulphocarbanilide, but all of the experiments gave negative results, only the decomposition-products of this addition-product being obtained. Certainly it is highly probable that such an addition-product is formed; but it is unquestionably very unstable, and, accord-

[1] Ann. Chem. (Liebig), **162**, 179. [2] *Ibid.*, **68**, 28.

ing to the temperature of the reaction, breaks down into succinanilic acid and phenyl mustard oil, or into succinanil, carbonic oxysulphide, and aniline.[1] The reaction in which succinanilic acid is formed may be explained by the following equations:

$$\begin{matrix}CH_2CO\\ |\\ CH_2CO\end{matrix}\!>\!O + C_6H_5NHCSNHC_6H_5 = \begin{matrix}CH_2NC_6H_5CSNHC_6H_5\\ |\\ CH_2COOH.\end{matrix};$$

$$\begin{matrix}CH_2NC_6H_5CSNHC_6H_5\\ |\\ CH_2COOH\end{matrix} = \begin{matrix}CH_2CONHC_6H_5\\ |\\ CH_2COOH\end{matrix} + C_6H_5NCS.$$

A number of experiments were also made to obtain the addition-product of phthalic anhydride and sulphocarbanilide, but these too yielded negative results. Although the temperature at which these reactions were tried was low and the time taken for the substances to combine was a number of hours, yet only the phthalanilic acid and phenyl mustard oil could be isolated.

The formation of an addition-product between the succinic or phthalic anhydride and sulphocarbanilide, although unstable and immediately giving decomposition-products, becomes highly probable on account of the isolation of a stable addition-product of maleïc anhydride and sulphocarbanilide.

Diphenylthiomaleïnuric Acid.—Equal molecules of maleïc anhydride and sulphocarbanilide were intimately mixed and ground to a fine powder. This mixture was heated in a small Erlenmeyer flask in an oil-bath. When the temperature of the bath was 80° the mixture began to melt. The temperature of the bath was raised gradually, and by the time the thermometer registered 95° the contents of the flask had completely melted and resolidified. This product was recrystallized from alcohol, from which it separates in bunches of short, flat, transparent prisms melting at 160°.

On analysis the following results were obtained:

0.2416 g subst.: 0.1744 g $BaSO_4$.
0.2052 g subst.: 16.3 cc. N (27° C., 754.3 mm.).
$C_{17}H_{14}N_2SO_3$. Calc. S, 9.82; N, 8.59.
Found S, 9.91; N, 8.80.

[1] This JOURNAL, 18, 340.

Diphenylthiomaleïnuric acid is readily soluble in acetone, very sparingly soluble in ether and chloroform; insoluble in benzene, ligroin, carbon bisulphide, and water. This acid forms crystalline barium, calcium, silver, potassium, and sodium salts.

If a mixture of maleïc anhydride and sulphocarbanilide is heated in an oil-bath to 180°, a small amount of carbonic oxysulphide is evolved, an evolution which becomes stronger if the temperature is raised to 200° or more.

Diphenylthiomaleïnuric acid is formed by the addition of maleïc anhydride and sulphocarbanilide, as follows:

$$\begin{matrix} CHCO \\ \| \quad >O \\ CHCO \end{matrix} + C_6H_5NHCSNHC_6H_5 =$$

$$\begin{matrix} CHCONC_6H_5CSNHC_6H_5 \\ \| \\ CHCOOH. \end{matrix}$$

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Contribution from the Kent Chemical Laboratory of the University of Chicago.

THE ACTION OF AMMONIA AND AMINES ON CHLORIDES OF SILICON.

BY FELIX LENGFELD.

Notwithstanding their importance and reactivity the chlorides of silicon have been little investigated. This is particularly noticeable when we consider the action of these bodies on nitrogen compounds and, more especially ammonia derivatives. Here we must expect interesting results, yet little has been done with silicon tetrachloride and even less with silicochloroform. Wöhler and Deville[1] obtained silicon nitride, Si_3N_4, by heating the product of the action of ammonia on silicon tetrachloride or silicochloroform. They paid little attention to the product before heating.

Schützenberger[2] also studied the action of ammonia on silicon tetrachloride. He likewise heated, in a current of hydrogen or ammonia without investigating, the bodies first formed.

[1] Pogg. Ann., **102**, 317; Ann. Chem. (Liebig), **104**, 256.
[2] Compt. rend., **89**, 644.

Persoz[1] considered the white substance formed when silicon tetrachloride absorbs ammonia to be an addition-product, $SiCl_4.6NH_3$.

Besson[2] has since confirmed Persoz's work so far as the composition is concerned.

Gattermann[3] obtained from silicon tetrachloride and ammonia a white powder which he considered silicon diimide, $Si(NH)_2$, or silicocyanamide, $NSiNH_2$. He indicated the possibility of getting from silicochloroform and ammonia hydrosilicocyanic acid, SiNH. Gattermann gave no analysis, and so far as I can see has published nothing further on the subject.

The action of aromatic amines on silicon tetrachloride has been studied by Girard and Pabst,[4] Hardin,[5] Reynolds,[6] Harold,[7] and Combes.[8] Girard and Pabst worked at high temperatures and obtained the products of secondary action only. Harden obtained the compound $SiCl_2(NHC_6H_5)_2$, and Reynolds the compound $Si(NHC_6H_5)_4$, from silicon tetrachloride and aniline and similar compounds from its homologues. Harold, working in Prof. Edgar F. Smith's laboratory, has shown that the difference in results is due to a difference in conditions. He considers the chlorine-free bodies formed by the action of excess of aniline on bodies of the type $SiCl_2(NHR)_2$. Combes obtained from parabromdimethylaniline with silicon tetrachloride the product, $Si[C_6H_4N(C_6H_5)_2]_4$, and with silicochloroform the product, $HSi[C_6H_4N(CH_3)_2]_3$, using sodium to remove halogen. He[9] also obtained from aniline and silico chloroform the compounds $HSi(NHC_6H_5)_3$ and $HSiCl(NHC_6H_5)_2$.

It seemed of importance to study the reactions of the chlorides of silicon further, and especially the reactions of silicochloroform. Silicochloroform was made by the method of Gattermann[10] slightly modified. Adopting the suggestion of Vigouroux,[11] the magnesium and sand were carefully dried

[1] Ann. chim. phys., **44**, 419.
[2] Compt. rend., **110**, 240.
[3] Ber. d. chem. Ges., **22**, 194.
[4] Bull. Soc. chim., **34**, 38.
[5] J. Chem. Soc., **51**, 40.
[6] *Ibid.*, **55**, 474.
[7] J. Am. Chem. Soc., **20**, 20.
[8] Compt. rend., **122**, 622.
[9] Compt. rend., **122**, 531.
[10] Ber. d. chem. Ges., **22**, 190.
[11] Ann. chim. phys. (7), **12**, 29.

and but a small excess of the latter used. This greatly increases the quantity of silicon that may be put into the combustion tube, and therefore the amount of silicochloroform from each charge. A more volatile chloride than silicochloroform seems to be one of the products of the reaction. It was not isolated. It is probably SiH_3Cl_3.

I have done considerable work on silico chloroform, but before drawing any conclusions have found it necessary to study some reactions of the tetrachloride and it is with these that this preliminary paper will deal.

Action of Ammonia on Silicon Tetrachloride.

In order to control the quantity of ammonia it was dissolved in anhydrous benzene and mixed with silicon tetrachloride in the same solvent. During the operation the apparatus was filled with dry nitrogen, air and moisture being carefully excluded. The flocculent white precipitate formed was forced by a current of nitrogen into a large adapter, used as a funnel. The adapter was plugged at the small end with absorbent cotton so that the precipitate could be washed with benzene or ligroin. The apparatus was so arranged that the washing could be done without admitting air.

When necessary the adapter was surrounded with hot water, the filter bottle connected with the pump, and a current of nitrogen passed over the precipitate at a temperature of 80°–90° and a pressure of 25–30 mm. The precipitate caked to such an extent that even under these conditions some wash-liquor remained. This could be removed by powdering in a mortar and again drying under diminished pressure, but this operation was attended with partial decomposition by the moisture of the air. Therefore analyses were made of products containing benzene or ligroin. Ligroin was frequently used for washing, but ammonia is too little soluble in petroleum ether to permit its use as a menstruum.

The following methods of analysis were used: Silicon was determined by treating the substance with fuming nitric acid and weighing the silicic oxide. To determine chlorine a portion was added to water, nitric acid, and silver nitrate, and allowed to stand over night. The precipitate was dissolved

in potassium cyanide and silver deposited electrolytically, or it was dissolved in ammonia, reprecipitated by nitric acid, and weighed as silver chloride. In the latter case a weighed portion was always reduced to silver to see if the silver chloride was free from silica. In every case it was pure.

Nitrogen was determined by adding water, distilling, and titrating the distillate with standard acid. The distillate was then returned to the distilling-flask, sodic hydrate added, and the ammonia again distilled and determined. From the latter titration the total nitrogen was calculated; from the former, that set free by water. The Dumas method could not be used, as ammonia came off before heating.

Seven grams (1 mol.) silicon tetrachloride was dissolved in 200 cc. benzene and to it added 5.6 grams (8 mols.) ammonia dissolved in 800 cc. benzene at 5°. After settling, 50 cc. of the clear liquid was drawn off and found to contain less than 0.25 milligram ammonia and no silicon. The action is therefore practically complete, and no soluble silicon compound is formed. The benzene was drawn off, the precipitate mixed so as to get it as nearly homogeneous as possible and an unweighed portion thrown into water. After two days the ammonia was distilled into $\frac{N}{10}$ sulphuric acid and titrated. The ammonium sulphate was returned to the distilling flask, potassic hydrate added, and the ammonia distilled and titrated. The ammonia formed by the action of water neutralized 27.5 cc. $\frac{N}{10}$ H_2SO_4, the total ammonia required 58 cc., or twice as much. The following reactions are therefore indicated:

$$SiCl_4 + 8NH_3 = Si(NH_2)_4 + 4NH_4Cl;$$

$$Si(NH_2)_4 + 4NH_4Cl + 4H_2O = Si(OH)_4 + 4NH_3 + 4NH_4Cl;$$

$$Si(NH_2)_4 + 4NH_4Cl + 8KOH = Si(OK)_4 + 8NH_3 + 4KCl + 4H_2O.$$

Silicon tetramide is a white solid. It is extremely unstable and cannot be dried, even at low temperatures, without losing ammonia and giving silicon diimide. It loses ammonia slowly at ordinary temperatures even under benzene. When ligroin is added to the fresh product, there is immediate evolution of gas and formation of silicon diimide. Silicon di-

imide, $Si(NH)_2$,[1] was obtained by Gattermann,[2] and probably by Persoz[3] and Besson.[4] The last two consider the product of the action of ammonia on silicon tetrachloride to be the compound $SiCl_4 6NH_3$. Analysis shows that not a single substance but a mixture is obtained. Unless carefully mixed the different layers do not give concordant results. This is not due to the action of moisture for if carefully mixed, different layers show no difference, even after a considerable time. The ratio of silicon to ammonia liberated by water is in different layers practically constant, while that of silicon to chlorine or to total nitrogen varies. This seems to indicate a mixture of silicon diimide and ammonium chloride in varying proportions. As the two could not be separated, analysis was made of the mixture as formed. Some freshly prepared substance was rapidly powdered and mixed in a mortar and dried for twenty-four hours in a current of nitrogen at 85° and 25 mm. It still contained some ligroin.

0.1202 g subst. : 0.1837 g Ag = 50.21 p c Cl.
0.2359 g subst. : 0.0489 g SiO_2 = 9.75 p c Si.
0.3288 g subst. : (with H_2O) 0.0366 g NH_3 = 9.16 p c N.
0.3288 g subst. : (with KOH) 0.1139 g NH_3 = 28.56 p c N.

$Si(NH_2)_4NH_4Cl$. Calc. Si, 10.29; Cl, 52.20; N (in imide), 10.29; N (in chloride), 20.59.
Found. Si, 9.75; Cl, 50.21; N (in imide), 9.16; N (in chloride), 19.40.

The analytical results seem not to agree with the reactions indicated. They sum up to only 96 per cent of the theory. This is due to the presence of about 4 per cent ligroin. Taking this into consideration, we get :

$Si(NH)_2.4NH_4Cl$. Calc. Si, 9.88; Cl, 50.11; N (in imide), 9.88; N (in chloride), 19.77.
Found. Si, 9.75; Cl, 50.21; N (in imide), 9.16; N (in chloride), 19.40.

This leaves little doubt of the composition of the mixture.

[1] I shall call this body silicon diimide though it may be silicocyanamide.
[2] *Loc. cit.* [3] *Loc. cit.* [4] *Loc. cit.*

The low yield of ammonia from imide is due to the action of moisture, as this sample was powdered in the air.

It was shown by a number of analyses of carefully mixed though moist precipitate that silicon diimide is the ultimate product if water and air are excluded. One-third the total ammonia was obtained with water. Selecting two analyses at random:

I. 0.3887 g subst. gave with water 0.03825 g ammonia and with potassic hydrate 0.1139 g ammonia = 8.1 per cent and 24.13 per cent nitrogen.

II. 0.4276 g subst. gave with water 0.04675 g ammonia, and with potassic hydrate 0.14025 g ammonia = 9.08 per cent and 27.24 per cent nitrogen.

The first action of excess of ammonia on silicon chloride in benzene is the formation of silicon tetramide and ammonium chloride. Silicon tetramide loses ammonia and gives silicon diimide, a white powder, decomposed by water, stable in the absence of moisture. It has not yet been separated from ammonium chloride, nor has its constitution been determined.

In order to prove that the action of ammonia on silicon tetrachloride is more than mere addition aliphatic amines were substituted for ammonia. The reactions of secondary amines on silicon chloride are more complicated than those of primary amines and will be treated of in a later paper.

Action of Ethylamine on Silicon Tetrachloride. Silicon Tetrethylamine.

Twenty grams of ethyl amine were dissolved in 400 cc. ligroin (b. p. 40°–60°) and 9 grams silicon tetrachloride in 50 cc. ligroin slowly added, the whole being cooled with ice-water. Ethyl ammonium chloride at once precipitated and was filtered from the solution. The ligroin was evaporated and the residue distilled under diminished pressure. Most of it came over at 102° under 20 mm. pressure. It contained silicon, nitrogen, carbon, and hydrogen, but no chlorine, and proved to be silicon tetrethylamine, the reaction being

$$SiCl_4 + 8NH_2C_2H_5 = Si(NHC_2H_5)_4 + 4C_2H_5NH_2Cl.$$

The silicon was determined by weighing some of the oil in a small bulb with capillary, breaking the capillary near the end,

dipping into alcohol, and alternately heating and cooling until all the oil had been washed out. A solution of sodic hydrate was added, the mixture allowed to stand two hours, and evaporated to dryness.

The silica was then determined in the usual way.

I. 0.310 g subst. : 0.0905 g SiO_2 = 13.67 p c Si.

II. 0.1812 g subst. : 44 cc. N (749 mm., 20°.5) = 27.43 pc N.

III. 0.2119 g subst. : 0.3664 g CO_2; 0.2233 g H_2O.

$Si(NHC_2H_5)_4$. Calc. C, 47.05; H, 11.76; N, 27.43; Si, 13.73.

Found. C, 47.14; H, 11.75; N, 27.43; Si, 13.67.

Silicon tetrethylamine is a colorless oil that does not solidify in a freezing-mixture. It keeps indefinitely in closed tubes, is decomposed by water, though not instantly, and is soluble in most organic solvents. Dilute nitric acid dissolves it without complete decomposition. It boils at 102° under a pressure of 20 mm.

NOTES.

The Hodgkins Medal.

This medal was recently awarded to Professor James Dewar of the Royal Institution, by the Smithsonian Institution. In the letter accompanying the medal, Professor Langley, the Secretary, says: "It gives me great pleasure to inform you, on the part of the Institution, that the first Gold Medal of the Hodgkins Foundation has been awarded to you in recognition of your indefatigable researches pursued for so many years, which have not only been potent in increasing and diffusing a more exact knowledge in regard to the nature and properties of air, but have opened the way for a practical utilization of this knowledge in the advancement of human welfare." Mr. Hodgkins became interested in the subject of the atmosphere through the beneficial results he experienced from the air of one of the New Jersey resorts. With the idea of increasing the benefits to mankind by the scientific study of the cause of such results he specified that the income from the fund should be used in promoting a knowledge of the atmosphere. It was from this fund that Lord Rayleigh and

Professor Ramsay were awarded $10,000 for their researches on the gases of the atmosphere. J. E. G.

Liquid Air Machines.

Another note, in the matter of the contested claims of Hampson, Linde, and Tripler as to the priority of their liquid air machines, has recently appeared, in a reply by Linde[1] to the statement made by Ramsay that Hampson's patent antedated that of Linde, although the principle made use of was the same in both. He calls attention to the provisional specification of Siemens, in 1857, for a combination of a cold air machine with an apparatus in which the compressed air could be cooled by the expansion of air, and to the patent granted to Solvay, in 1885, for an improvement on the principle used by Siemens. In May, 1895, Hampson, in his provisional specification, says: "The usual cycle of compression, cooling, and expansion, is modified by using all the gas after its expansion to reduce as nearly as possible to its own temperature the compressed gas which is on its way to be expanded." No mention is made of the ideas of Siemens or Solvay nor of the application of the Thomson-Joule effect. From the 20th to the 25th of May, 1895, Linde was exhibiting his machine in Munich and was making liquid air by the liter. His machine was described in the Journals in September, 1895, while it was not until April, 1896, that Hampson handed in the patent specifications, in which now the Thomson-Joule effect was given as the source of cold. J. E. G.

Gases of the Argon-Helium Type.

In a recent number of the Berichte[2], Bohuslav Brauner contends that the position taken by the majority of chemists in accepting the gases discovered by Ramsay as elementary monatomic substances, and in attempting to find places for them in the Periodic System, is not justified by the results reached in the investigations of their nature and properties. He considers it his duty to emphasize the objections, which have been offered by himself and others, to these views, although he is almost the only one, of a number who at first hesitated to accept Ramsay's ideas, who still denies the justice of the claims. He starts out by assuming that metargon contains carbon, on account of its peculiar spectra, and as Ramsay bases his opinion of its monatomic condition on the factor 1.66 as obtained from the ratio of specific heats, he argues that this figure cannot serve as a criterion for monatomicity since it is obtained in the case of the compound gas metargon. He

[1] Ber. d. chem. Ges., **32**, 925. [2] *Ibid.*, **32**, 708.

considers the inactivity of these gases another strong argument against their atomic condition, for it is generally found that substances are most active in the atomic condition. He suggests again the possibility of the atoms being so firmly and closely held together that they show no internal vibration and act as a monatomic gas. While commending the remarkable work of Ramsay, he considers that the work only justified the conclusion that he was working with extremely interesting inactive compounds or allotropic modifications of substances already known, rather than with a series of new elements. He also quotes a recent paper by Piccini[1] in support of his view. In this paper the author contends that there is no place in the Periodic System for the new gases, where their position and properties can be reconciled, nor are the atomic volumes or boiling-points what they should be to conform to the generalizations as expressed in the curves of atomic volumes and of boiling-points. J. E. G.

REVIEWS.

A Select Bibliography of Chemistry, 1492–1897. By H. Carrington Bolton. First Supplement. Smithsonian Institute. 1899.

In 1893 Professor Bolton published a bibliography of chemistry which contained about 12,000 titles, under the following heads: Bibliography, Dictionaries and Tables, History of Chemistry, Biography, Chemistry, Pure and Applied, and Periodicals. In this supplementary volume he has added more than 5,000 titles of books published since 1893, or before unknown. Professor Bolton has a special fondness for the historical and bibliographical side of chemistry, and has published a number of papers of his researches in these lines, a kind of work which is very desirable and necessary and for which comparatively few have the patience and systematic habits. Besides his own researches carried on in the libraries abroad and in this country, the author had the cooperation of a number of chemists who supplied lists of the publications of their respective countries. J. E. G.

The Free Expansion of Gases. Translated and edited by J. S. Ames, Ph.D., Professor of Physics in Johns Hopkins University. 75 cents.

Prismatic and Diffraction Spectra. Translated and edited by J. S. Ames, Ph.D. 60 cents.

Röntgen Rays. Translated and edited by George F. Barker, LL.D., Professor of Physics in the University of Pennsylvania. 60 cents.

The Modern Theory of Solution. Translated and edited by Harry C. Jones, Ph.D., Associate in Physical Chemistry in Johns Hopkins University. $1.00 Harper & Brothers, New York and London. 1898.

An idea of the general field which this series, edited by

[1] Ztschr. anorg. Chem., 19, 295.

Joseph S. Ames, Ph.D., Professor of Physics in Johns Hopkins University, is expected to cover, can perhaps be best obtained from extracts from announcements of the publishers.

"This series will embrace a large number of translations and reprints of the most important articles which have been written in the history of science, including many which have an important bearing upon the present state of science. The fields of physics, astronomy, chemistry, and probably other sciences will be covered." "This series will lay before the general reader the original statements of many of the more important theories and experiments which until now have not been readily accessible."

Many of the original papers, published by the chemists of the last century and the early part of this one, which contain results upon which the present theories of chemistry are founded, have been rendered accessible to everyone through the efforts of Professor Ostwald, who has edited reprints of a number of these papers under the general title "Ostwald's Klassiker der exakten Wissenschaften." In a similar series published in England under the title "Alembic Club Reprints," we find a number of the most important articles that were published in English journals, such as those of Davy, Dalton, Faraday, and Priestley.

In this present series, as stated in the announcement, more than one science is to be included, though the volumes so far announced only include those in the field of physics and physical chemistry. In the first three volumes, which have already come to hand, we have the important papers by the following authors: in the first by Gay-Lussac, Joule and Thomson; in the second by Fraunhofer; and in the third by Röntgen, Stokes and Thomson. These numbers also contain notes by the editors and biographical sketches and bibliographies. In the volume on "The Modern Theories of Solution," in which the chemist is more especially interested, we find translations of the papers which are the foundation stones of the present theories of physical chemistry and which have bridged the chasm between the domain of the physicist and that of the chemist. In it we find the articles by Pfeffer on "Osmotic Investigations," by Van't Hoff on "Osmotic Pressure," by Arrhenius on "Dissociation of Substances Dissolved in Water," by Raoult on "The General Law of the Freezing of Solvents," "On the Vapor-Pressure of Ethereal Solutions," and "The General Law of the Vapor-Pressure of Solvents." The value of these articles is further increased by the general review of their influence on the development of the science and by the valuable

bibliography covering the subjects of Osmotic Pressure, Theory of Solution and Changes in Freezing-Point and Boiling-Point caused by Dissolved Substances. No one can fail to recognize the great importance of a knowledge of the work of others as acquired from a study of these original records, to enable one to get in touch with the writer and to see with his eyes and hear with his ears so far as possible, instead of through the biased or misstated records of opponents or competitors. These volumes are published in a very neat and attractive form and can be recommended as valuable supplements to text-books on the subjects treated of in this series.

J. E. G.

TRAITÉ D'ANALYSE CHIMIQUE QUANTITATIVE PAR ELECTROLYSE. By J. RIBAN, (Paris). [Masson et Cie. 1899. pp. VI, 304].

Since Gibbs and Luckow first used electrolysis as a means of quantitative determination thirty-five years ago, this application of electricity has steadily risen in favor. Many eminent chemists have given time and thought to the detailed study of special cases, and it is pleasant to see that Professor Riban is familiar with a wide range of this literature. The works of Classen, Smith, Neumann, Riche, Freudenberg, and others are freely quoted in the book under discussion, without however giving either reference or date. The omission is much to be deplored, but its detrimental effect is somewhat diminished by the very full re-statement of the methods and data. Indeed the repetition frequently leads the author into masses of unessentials which somewhat encumber the main thread of the argument.

The book is divided into four parts, of which the first recounts the physical laws underlying the practice of electrolysis, as well as the apparatus necessary to produce and to utilize galvanic energy. Some of the description is particularly clear and to the point, but it is not free from occasional error. The most incomprehensible mistake is the adherence to the old idea that the total heat of a reaction is convertible into electrical energy, in spite of the fact that M. Riban has evidently seen the equation of Helmholtz. A recent description of the theory of electrolytic separation with no allusion to the illuminating hypotheses of Arrhenius and of Nernst is indeed an oddity, but it is to be encountered here. On the practical side the book is much more trustworthy, recommending the dynamo and accumulator as usually the most convenient fountain of energy, and describing in minute detail every conceivable form of anode and kathode. While most of the connections recommended are good, the switch-board pictured on page 126 is a tempting invitation to a short-circuit, that sub-

tle trap always waiting for the uninitiated. The gas-"voltameter" is scarcely condemned in strong enough language, and the grave inconvenience involved in the use of a series-dynamo for charging cells might be emphasized more trenchantly.

It is unfortunate that most writers upon electrolytic analysis, M. Riban among the rest, dwell upon the accidental voltage existing between the electrodes while the current is running as an important factor in the case. This voltage is of course made up of two quantities, the normal fall of potential due to the unknown resistance of the solution, and the "polarization" of the cell. The polarization is really the essential question; it varies with the metal to be deposited, and is the only sure criterion for determining what substances are to appear in the elementary state. If the resistance and current strength were known, the polarization could of course be calculated with ease, from the total potential registered by a voltmeter; but the analyst does not usually have any knowledge of the ever-changing resistance in his cell. Hence the determination of the "Klemmspannung" is rather an idle sport. The plan, so much condemned by Classen, Riban, and others, of using as the source of current a galvanic cell with a potential between those of the polarizations corresponding to two metals to be separated is really a safer one, if the electrolysis is to run without constant supervision.

The three remaining parts of the book treat of individual determinations, of separations, and of technical applications respectively. One is glad to find that the author, besides recounting most of the methods which have been proposed, sometimes criticises them upon the basis of his own experience. A still rarer virtue is to be found in the occasional advice to use ordinary gravimetric methods rather than electrolytic; for enthusiasm about the frequent real advantages of electrolysis sometimes leads chemists to apply electrolytic methods to cases better treated in other ways.

During the perusal of this detailed part of the book one asks one's self continually the question "Why?" In fact, very many problems remain still to be studied concerning the mechanism of deposition in complex solutions, but M. Riban has by no means explained all which now seem explicable. For instance, he has failed to call attention to Foerster's admirable explanation of the deposition of cuprous oxide from neutral solutions of cupric sulphate. The chapter dealing with technical applications occupies only 29 pages and is very incomplete. The presswork and illustrations are in characteristically admirable French style.

In short, this volume is not an unmixed success; and while

in France it may take the place of the works of Neumann, Classen and Smith, it will not be likely to supplant them in the laboratories of America, England, and Germany. As a record of evident practical experience with many of the methods it is distinctly of value. T. W. R.

EXAMINATION OF WATER (CHEMICAL AND BACTERIOLOGICAL). By WILLIAM P. MASON, Professor of Chemistry, Rensselaer Polytechnic Institute. New York: John Wiley & Sons; London: Chapman & Hall, Limited. pp. 135. 1899.

A useful practical manual of water examination for sanitary purposes, in which not only the methods for making the several determinations are explained at length, but general remarks, sensible and well balanced, are made on the interpretation of these determinations, the relative importance to be attached to them, and the collateral facts to be weighed in connection with them. Various special cases occurring in the experience of the author are referred to, which are interesting and instructive, for example, on p. 47, the finding an unusually large amount of nitrates in the water of a deep rock-drilled well, traced to the fact of fifty pounds of nitroglycerine having been used to "torpedo" the well.

It might perhaps have been well, in the second part of the manual, to have given a little more of general matter on bacteria and their relations to health and disease, and to have insisted a little more strenuously on the very special precautions necessary in the collection, preservation, and transport of water samples, to render a bacteriological examination of any value. J. W. M.

DAS LEITVERMÖGEN DER ELEKTROLYTE, INSBESONDERE DER LÖSUNGEN, METHODEN, RESULTATE, UND CHEMISCHE ANWENDUNGEN. VON DR. F. KOHLRAUSCH, Präsident der physikalisch-technischen Reichsanstalt, und Dr. L. HOLBORN, Mitglied der physikalisch-technischen Reichsanstalt. Mit in den Text gedruckten Figuren und einer Tafel. Leipzig: Druck und Verlag von B. G. Teubner. 1898. pp. 211.

We are especially fortunate in having a work on "conductivity," from the same hand which devised the method for determining the power of solutions of electrolytes to conduct the current. The book deals with the subject in a broad way, and contains just such information as is needed by every one who would make conductivity measurements. Chapters are devoted to: instruments and methods of measuring conductivity; methods, using the alternating current; solutions; temperature; and chemical applications of the conductivity of aqueous solutions. A complete bibliography of the literature on conductivity of electrolytes, is followed by tables of results obtained.

The discussion of the forms of apparatus which can be employed is well illustrated by drawings, and the more common sources of error in measuring conductivity with the alternating current, are pointed out in detail. The results given, are referred to a common standard of resistance, that of a cube of the substance whose edge is 1 cm. long, and are therefore directly comparable. The work is, as we should expect from its authors, beyond criticism, and cannot be commended too heartily to all who are interested in conductivity work.

H. C. J.

JAHRESBERICHT ÜBER DIE FORTSCHRITTE DER CHEMIE. LIEBIG UND KOPP. Für 1892. Viertes Heft.

This is the last part of the first volume for 1892 and contains the table of contents. It covers the field of general, physical, and inorganic chemistry, and a part of organic.